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PROGRESS IN DEVELOPMENT OF LOW DENSITY
POLYMER FOAMS FOR THE ICF PROGRAM

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Table of Contents

I.	Foam Program Overview	(R. Morgan)
II.	A. Foams by crystallization gelation	(L. Lucht and S. Letts)
	B. Computer simulation studies of polymer gelation	(R. Cook and M. Mercer)
III.	Emulsion Polymerization	(S. Letts and M. Litt)

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21

PROGRESS IN DEVELOPMENT OF LOW DENSITY POLYMER
FOAMS FOR THE ICF PROGRAM*

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ABSTRACT

This report describes the status of CH foam development with densities of 50 mg/ccs and cell sizes of 1 μ m for the ICF Program. Two approaches that both involve polymer phase separation are being investigated. The first involves a gelation-crystallization of high molecular weight polyethylene from solution, whereas the second approach involves the modification of the phase separation morphology of water-styrene emulsions by molecularly-tailored surfactants followed by polymerization of the continuous styrene phase.

I. FOAM PROGRAM OVERVIEW

R. J. Morgan

The ICF Program has a need for low density CH materials with a density of 50 mg/cm^3 and cell sizes of $1 \text{ } \mu\text{m}$. Burnham and Brown¹ at LLNL have conducted a survey of 33 available foam candidates fabricated internally in DOE and, also, commercially. A summary of foam cell sizes and densities are illustrated in Figure 1. It was concluded from this survey that the ICF density and cell size requirements for CH polymeric foams were not within the state of the art.

To produce CH foams with the characteristics required for ICF targets, two approaches were initiated, namely foam formation via (i) crystallization-gelation (See Section II) and (ii) emulsion polymerization (See Section III).

The gelation crystallization process involves dissolving high molecular weight polyethylene in a solvent such as tetralin and forming an entangled macromolecular gel above the polymer crystal melting point. From controlled cooling of such solutions to maximize the concentration of crystalline nuclei, foams that meet the ICF requirements have been produced after supercritical extraction of the solvent. Such polyethylene foams are machinable but are too soft to maintain stringent dimensional stability requirements. As such, we are presently attempting to stiffen such foams by enhancing crystallization of the polymer amorphous regions via combined thermal-radiation treatments.

The emulsion polymer process to produce small cell size, low density foams is underway at Case Western University. This program involves the synthesis and characterization of surfactants for water in styrene emulsions. The stability of these emulsions as a function of temperature, surfactant concentration, styrene volume and methods of emulsification and polymerization will be investigated. After styrene polymerization and evaporation of the water polystyrene foams of the required ICF characteristics will be produced.

We consider the principal problem involved in developing small cell size/low density CH foams is the ability to produce structures with good mechanical stability. The mechanical integrity is maximized with networks of stiff, fully crystalline rods or flakes interconnected by crystalline regions. Our continuing development efforts will consider approaches to produce stiffer foams.

The two principal approaches in this advanced foam development program are now described in more detail in Sections II and III.

II A. FOAMS BY CRYSTALLIZATION GELATION

Lucy Lucht and Steve Letts

Introduction

We discuss in this section the work done to develop a CH based foam for use in the LLNL ICF program.

The technique we are using is crystallization gelation of polyethylene solutions, induced by changing the temperature of the system, and subsequent removal of the solvent by supercritical extraction. Gelation of polymer/solvent systems is a phase separation, which can also be induced by chemical cross-linking. However, chemical cross-linking, while producing a gel with permanent links between the polymer chains, usually yields a gel which shrinks considerably during solvent extraction. The foam collapses, and the low density, high-pore-volume material we desire is not achieved.

For gelation by crystallization to occur, the polymer chains must be long and in a high enough concentration for the chains to be entangled. We thus make a highly concentrated solution of polyethylene so that entanglement of the polymer chains occurs. The chains crystallize and fall out of solution when the system temperature is decreased or its pressure changed. Crystalline lamella then form at points of entanglement. The final structure is a cross-linked network, where the junctions are crystalline lamella and the chains are crystalline fibers. Such a structure has rigidity due to its high crystallinity, and will not be destroyed unless raised above its melting point. Thus, the crystals

which form are thermally reversible cross-links.

The physical properties of the foam resulting from gelation by crystallization depends on the specific types and sizes of crystals formed, the percentage of the polymer chains which crystallize, and the extent that the crystals either overlap or are part of the same crystal. These properties in turn depend on the molecular weight and degree of branching of the polymer, the interaction of the polymer with its solvent, whether or not the polymer/solvent was in thermodynamic equilibrium prior to gelation, the rate of cooling to crystallize, the temperature of crystallization, and the time allowed for crystallization.

Polyethylene (PE), polyethylene oxide (PEO), and polyvinylidene fluoride (PVF) were all considered for gelation. We chose to concentrate mainly on PE because it is a pure CH polymer, is available in linear, high molecular weights of up to six million, and is easily crystallizable. The first part of this section discusses our work on polyethylene. In the second part, we discuss gelation experiments with PEO.

Foams from Ultra-High Molecular Weight Polyethylene. To make low density polyethylene foams, we mix at 130 to 160 C a 1 to 5 wt/vol % solution of very high molecular weight polyethylene, on the order of a million repeating units, in the desired solvent. Then we cool the solution to crystallize the polyethylene, and form the highly entangled gel. Solvent is removed from the gel by supercritical extraction, leaving behind a low density foam.

Dissolution. To dissolve polyethylene, the solvent should have a solubility parameter on the order of 8 Hildebrands $(\text{cal/cm}^3)^{1/2}$ and

be a poor hydrogen bonder. Higher molecular weight polyethylene requires longer times to dissolve. In addition, vigorous stirring of high molecular weight polyethylene in solution aligns the polymer chains. They actually come out of solution.

We found that dissolution of very high molecular weight polyethylene, I.V. =16, 20, and 29, corresponding to molecular weights of approximately 2 million, 3 million and 6 million, respectively, could be achieved under the following conditions:

1. Solvents must be of a non-polar nature, and poor hydrogen-bond agents. These include alkanes (n=7-12); some long-chained alkenes, 1-octene, 1-dodecene; hydroaromatics and aromatics, tetralin, decalin, xylene, toluene, naphthalene, biphenyl, nitrobenzene, ethyl benzene; and cyclohexane. The solubility parameters, structures, molecular weights, and boiling points of these solvents are shown in Table 1.
2. Solvents must be at temperatures of about 130 C, except for nitrobenzene, which must be at 215-220 C.
3. Conditions must be quiescent, with either slow addition of the polyethylene or all at once.
4. 1-3 days are required.
5. Concentrations were less than 10 wt % polyethylene. It may be possible to achieve higher concentrations.

Dissolution was not achieved under these conditions:

1. with agitation or stirring.
2. with polar solvents, such as amyl acetate.
3. at temperatures less than the equilibrium melting point of the mix, greater than 110 C in general.

Gelation: Once dissolution is achieved, the mix must be ramped thermodynamically to phase separation or crystallization, which may coincide. This step probably determines the final morphology of the foam, so the effects of solvent, polymer molecular weight, rate of cooling to crystallization, temperature of crystallization, and time of crystallization are quite important.

The solvent affects the end-to-end distance of the individual polymer chains, and thus, the degree of the entanglement of the chains in concentrated solutions. The degree of entanglement in turn determines the cohesiveness of the gel, and undoubtedly affects the types of crystals formed, which partly determines the strength of the gel. The solvent is also important in the initial formation of crystal nuclei. We can understand this as a surface energy issue. The formation of crystalline nuclei requires energy because new surfaces are being created, so a certain amount of subcooling is required, even though the crystalline form of polyethylene is more thermodynamically stable once formed. Thus, the interfacial surface energy at the crystal face/solvent boundary strongly influences the rate of crystal formation and the temperature of initial nuclei formation.

To investigate the effect of these variables on gelation, we visually measured the cloud points, determined the dissolution temperatures, took optical micrographs, and performed differential scanning calorimetry (DSC) scans of several PE/solvent systems.

The cloud point data are shown in Figure 2 as temperature vs wt %. There are two curves, separated by 5 to 10 C over 0 to 10 wt % PE in solution. The visual melting temperatures of the gels are 117-140 C for

n-alkanes and 112-135 C for aromatics and hydroaromatics plus 1-octene. Thus, the amount of subcooling for n-alkanes is 32-55 C at 0.5 wt % and 22-45 C at 9 wt %; for aromatics and hydroaromatics, the amount of subcooling is 42-64 C at 0.5 wt % and 27-49 C at 9 wt %; for 1-octene, subcooling is 27-49 C at 0.5 wt % and 17-39 C at 9 wt %. For the high concentrations, there is enough overlap in the data that no conclusions can be drawn. But at the lower concentrations, we conclude that it requires more energy for the nuclei to be formed in the aromatic/hydroaromatic solutions.

Some general observations may be made about the gels. Gels formed from the alkanes tended to be more soupy and less cohesive than those formed from cyclic solvents, especially tetralin and decalin. The gels were centrifuged at 1000 g's to determine the amount of free solvent. The results of the centrifugation were that the alkane gels, even at 5 or 10 wt % polyethylene had about half their volume in free solvent, whereas similar gels in tetralin or decalin appeared to have little free solvent and were not significantly compressed. This could be due to either the smaller density difference for the PE vs tetralin/decalin solvents or possibly more extended chains in the PE solvent. It is also apparent that the molecular weight of the PE has an effect on the quantity of free solvent. That is, the PE of intrinsic viscosity (I.V.)=20 dl/g in general has less free solvent than the cuts of I.V.=16 or 29 dl/g. It may be that a minimum number of chain ends is required to achieve sufficient entanglement.

Thin smears of the gels from decane, dodecane, decalin, tetralin, 1-octene, and xylene were observed under cross-polarized light on the

optical microscope. The optical micrographs of the smears are shown with SEM's of their foams in Figures 3 and 4. The crystalline morphologies are quite different. Gels from decane and dodecane have obvious spherulites, on the order of 20 to 50 μm in diameter, while those from p-xylene, 1-octene, decalin and tetralin have a smaller crystalline morphology. The crystalline morphology matches fairly well the surfaces as viewed with the electron microscope, except for xylene gels.

Quench Rate and Temperature of Crystallization: The entangled chains and macromolecular chains take time to rearrange, so if the temperature at which crystallization would begin is rapidly bypassed, the degree of subcooling can be made very large. The lower the temperature is below the temperature of crystallization, the more nuclei are formed and the smaller the nuclei. In principle, a smaller crystalline morphology can be obtained. Figure 5 shows differential scanning thermograms of pure PE, I.V.=20, quenched from the melt at 10, 20, 30 and 60 C/min. The temperature of crystallization drops, from 118 to 116 to 114 to 108 C. The change in the temperature of crystallization with quench rate depends upon the rate of diffusion of the polymer in its environment. We have observed that more rapid cooling of dodecane and decalin gels results in smaller crystal structure, but has less effect on tetralin or xylene gels, whose morphology is generally small. This implies that the rate of diffusion of the polymer in tetralin and xylene is less than in dodecane.

Removal of Solvent. We use supercritical extraction to remove the solvent from the gel without collapse. In supercritical extraction, the extracting solvent is taken above its critical temperature and pressure.

The resultant fluid has solvation properties similar to its subcritical liquid, but without gas/liquid interfacial tension and a low fluid viscosity, similar to its subcritical gas; thus, it is a good solvent that passes no disruptive meniscus through the gel during extraction. From this process, the gel is sealed into a pressure chamber, and the system is filled with liquid carbon dioxide. Liquid carbon dioxide is flushed through the chamber for 1-2 days to allow complete solvent removal. Then the chamber is raised above the critical pressure, 75.3 atm, and critical temperature, 31 C, of carbon dioxide. The pressure is slowly released so that a liquid meniscus never passes through the material.

The solubility parameter range of supercritical carbon dioxide is 6 to 8 Hildebrands, while the solubility parameters of the gelation solvents range from 7.7 to 9.5 H. Carbon dioxide is also a nonpolar fluid, so it is a good flushing agent for the solvents being used. Plastic collapse of the foam is also avoided, since at 40 C and pressures greater than 75 atm, the polyethylene remains crystalline.

We have made several polyethylene foams by supercritical extraction of the gelation solvent:

1. a 50 mg/cc foam from a tetralin gel. The foam piece was 1/2 inch in diameter and approximately 1 inch long. It showed good cohesiveness and could be handled without collapse. The void diameters ranged from 1 to 10 microns.
2. a 65 mg/cc foam from a dodecane gel and a 60 to 70 mg/cc foam from a decane gel. These gels were formed in a jacketed reactor, were on the order of 2 inches in diameter and 1 1/2 inches deep. Both foams tended

to be crumbly on cutting. The structure shown in Figure 3 is representative of the foams made from alkane gels. There are spherulitic balls of 20 to 50 μm , with an internal structure similar to that of tetralin, where the void diameters are 1 to 10 microns.

3. a 70 mg/cc foam from a xylene gel and a 80 mg/cc foam from a 1-octene gel. These gels were made in sealed ampules, and are about 1/2 inch in diameter and 1 inch in length. As with the foam from tetralin gels, these foams have good cohesiveness.

The rate of mass transfer of the solvent out of the gel during flushing is also important, as a foam from a tetralin gel illustrates. The foam was removed from the supercritical extraction apparatus before the gelation solvent was completely gone. The foam collapsed during subsequent vacuum drying due to surface tension. In future experiments, we will pass the effluent from the SCE apparatus through a gas chromatograph to ensure that solvent is removed.

Discussion/Summary. We have shown that low density polyethylene foams of 50 to 100 mg/cc with void diameters as small as 2 to 5 μm , on the average, can be made. Gelation studies using cloud point measurements, dissolution temperature measurements, optical microscopy and DSC have indicated that the cell size is reduced by rapid thermal quenching and strongly affected by solvent choice. At this point, the best foam candidates are from gels of UHMW PE 1900, I.V.=20, in tetralin, xylene or 1-octene. These foams have void diameters on the order of 2 to 5 μm . Tetralin appears to be the most cohesive foam, showing no friability. Complete removal of the solvent during SCE is important, as some foams have shrunk and been found to still contain about 50 % solvent.

Foams From Polyethylene Oxide. Polyethylene oxide (PEO) is the second crystallizable polymer we have investigated as a gel forming polymer from which a foam can be made by extraction of the solvent. With PEO two other processing techniques were investigated: gamma radiation induced crosslinking, and removal of solvent by freeze drying. PEO is available in a range of molecular weights up to 5×10^6 g/mole. At this high molecular weight significant polymer chain entanglement, and thus gel formation, occurs at relatively low polymer concentration in solution.

There are two ways to induce gelation: dissolution of a high molecular weight polymer, and cross linking polymer in solution. Both of these techniques were investigated for PEO. Both high and low molecular weight PEO were dissolved in water, which is a good solvent for PEO, over a concentration range from 1 to 5 percent. The high molecular weight solution gelled at even 1 percent. The low molecular weight solution formed a thick solution which did flow. The solutions were next exposed to cobalt-60 gamma radiation for doses from one to 50 Mrad to initiate crosslinking. All solutions gelled after exposure to the radiation. Two effects of high radiation doses were noted: hydrogen bubbles are generated within the gel from degradation of the polymer, and the polymer gel shrank as increased crosslinking occurred. The optimum dose may be less than 1 Mrad, however, which was the lowest dose investigated.

The solutions were next frozen by immersion in liquid nitrogen. The frozen solution was finally dried by freeze drying in a vacuum system. A typical freeze dried PEO foam is shown in Fig. 6. Cell size was from 2 to 10 microns. The sample showed good uniformity over the entire sample which was approximately 1 centimeter in size.

II B. COMPUTER SIMULATION STUDIES OF POLYMER GELATION

Robert Cook and Michael Mercer

Introduction

Low density polyethylene foam materials can be made by the gelation of high molecular weight polyethylene from a 5% solution in a suitable solvent, followed by solvent exchange with liquid CO_2 and super-critical extrusion of the CO_2 . Experimental work along these lines is being conducted by Lucy Lucht at this Laboratory. The morphology of the foam will be controlled to a large extent by that of the gel. The process of gelation in these systems is not well understood. We would like to have a better understanding of the dynamics of gelation and its relationship to gel morphology. To this end, in support of Lucht and other experimental efforts in the Target Fabrication group, we have initiated a program to simulate the gelation of chain molecules from solution. It is not our intention in that work that follows to model in any detail the features of polyethylene, except that it is a chain molecule. We expect that the general features of gelation depend largely upon this feature. It would, in fact, be unprofitable at this time to attempt a detailed model of polyethylene, not only due to the enormous computational time required for such a model, but also because the detail would in all likelihood obscure the basic physics of aggregation of chain molecules. It is these features that we plan to explore in this initial study. A better understanding at this level can help guide the experimental efforts.

Briefly our intention is to model the polyethylene system with a number of chains of particles situated in a box at an appropriate density. By solving the equations of motion for the particles in the system, while slowly extracting the thermal energy, the system should "gel". This is due to local condensation of adjacent entangled chains into small regions at unit density which are connected to one another by elongated tie chains. Our goal is to understand as much as we can about the dynamics of this process and the variables that control the gel morphology.

The model we are using consists of a number of simple bead-spring chains. No bond angle potentials are included at this point. As shown in Fig. 7, the interaction between non-adjacent beads, either on the same chain or on different chains, is by a relatively short range potential of the form

$$E_{i,j} = \frac{a}{r_{i,j}^m} - \frac{b}{r_{i,j}^n} \quad (1)$$

for non-adjacent beads i and j which are separated by a distance $r_{i,j}$. Adjacent beads on the same chain interact by simple Hookean springs of energy

$$E_{i,i+1} = \frac{1}{2}k(r_{i,i+1} - r_0)^2 \quad (2)$$

For the explorator, work presented here, $m = 6$ and $n = 3$, and the constants a and b are picked so that the potential minimum of Eq. (1) is at $r_{i,j} = r_0$, and the curvature at the minimum is equal to k . Other choices of a more realistic nature are possible and are being explored.

In this initial effort, however, we desire to keep the situation as simple as possible. The value of r_0 is taken as unity. The initial state of the system is created by taking a specified number of particles, N , and dividing them into n chains of N/n atoms each. These chains are then placed in a cubic box in a random fashion. Certain constraints are imposed: specifically all $r_{i,j}$ are required to be greater than r_0 and all $r_{i,j+2} > 3r_0$. This second requirement is imposed only on the initial condition to achieve a fairly extended and thus entangled initial configuration. To avoid edge effects, periodic boundary conditions are applied. This effectively means that if a chain leaves one side of the box it immediately reenters on the opposite side. We will expand upon the ramifications of these conditions shortly. The size of the box is determined by the desired particle density p . Thus the side length, l , is given by $l = (N/p)^{1/3}$. The work presented here is for $p = .05$.

Once the initial configuration is established, we commence a numerical solution of the $3N$ coupled equations of motion for the system in order to follow its evolution in time. To mimic cooling, we slowly extract energy from the system by adding a velocity damping term to the equations of motion which slowly extracts thermal energy from the system. This is not the same as controlling the temperature, a problem that is discussed later. The simulation is run until the system stabilizes.

Results and Discussion. Our initial simulations on systems of five chains of 20 particles each gave only collapse into a single cluster of unit density due to insufficient entanglement. This was to be expected, since the chain length was very short. An analogous situation occurs

with low molecular weight polyethylene which does not form good foams. With five chains of 100 particles each we were able to obtain a stable network structure with five or six clusters of particles connected by stretched chains. It should be emphasized that the periodic boundary conditions play a key role in the calculation in terms of stabilizing the structure because they eliminate surfaces which would allow for collapse. Though artificial in a sense, one must remember that we are modeling only a relatively few particles compared to that in a macroscopic sample, and that the box is only on the order of a few tens of angstroms on a side. We thus imagine our box embedded in the middle of a sample, and the periodic boundary conditions are the best representation of the surrounding environment. The only condition that must be met is that the effective range of the pair interactions be significantly less than the dimensions of the box. This is certainly the case in the work presented here.

The data presented here is for a 2500 particle system of five chains. In Fig. 8a we show the initial configuration of the chains which are distinguished by different colors. The box is drawn in pink. Note that the red chain appears in two pieces. This is a visual artifact due to the periodic boundary conditions discussed earlier. The red chain actually leaves the top of the box and reenters at the bottom. The yellow chain appears in many pieces, particularly on the right due to repeated passage through the box wall.

Figures 8b-d show the progression with time. Note in Fig. 8b the developing local clusters which become more clearly defined in Figs. 8c and 8d. As the clusters grow by pulling in loose chains, a process

which models the initial crystallization of polyethylene in gel formation, the connecting chains become straight and somewhat stretched. The development of open spaces or pores between the clusters can also be seen. The size and distribution of these may depend upon the rate of energy removal. Studies are under way.

In order to quantify the evolution of the network system, we have calculated the radial distribution function which essentially measures the way the average density of particles varies as we move radially away from an average particle. In Fig. 9 we have plotted this function for the four configurations shown in Fig. 8. Peak heights at short distances are off scale. Note that for the initial configuration the distribution peaks near $r = 1.0$. This corresponds to the equilibrium bond length r_0 , since every particle, except those on the chain ends, has at least two neighbors at this distance. Smaller peaks also appear at distances of about 1.9, 2.8 and 3.6 corresponding to the second, third and fourth neighbors along the chain. The values are less than integral multiples of the equilibrium bond length due to bending of the chain. There is then a fairly smooth drop off to the bulk density value of 0.05. By the time corresponding to Fig. 8b there has been a marked increase in the density at small distances due to the beginning of cluster formation. This increase in density comes at the expense of the density in the $r = 4$ to 8 region. Essentially the initial collapse is only a local phenomenon. At longer times corresponding to Figs. 8c and 8d, when the network structure is fairly well defined, the densities at short distances become very high due to the close packing in the clusters. This increase now comes at the expense of the density at distances in the

$r = 5$ to 13 region. The small hump in this curve at about $r = 14.5$ may be due to some average spacing between clusters, and if so is indicative of a system "pore size". This feature is currently under examination.

It is our intention to refine the model so as to include several features that have been ignored. Most importantly, our method of cooling the system by damping the velocities is at best artificial. We would like to be able to directly control the temperature of the system and plan to accomplish this by modifying the program to include the random Brownian motion effects of the solvent, which are directly temperature dependent, by a Brownian dynamics solution to the equations of motion. Briefly this involves the addition of a random, though statistically temperature dependent, force term to the velocity-damped equation of motion. This would allow for the direct temperature control of the system. Additionally we plan to modify the potentials used to better represent realistic polymer potentials by the inclusion of a bond-angle potential. This can be done with little increase in computational time.

Conclusion. We have discussed a program aimed at developing a better understanding of the gelation of polymers from solution. Through appropriately designed computer simulation experiments, we can follow the dynamics of gel formation and can explore some of the variables that effect critical properties such as pore size. Information of this nature can be important in offering guidance to the on going experimental effort.

III. EMULSION POLYMERIZATION

S. Letts (LLNL and M. Litt (Case Western Reserve University)

An approach distinctly different from using crystalline polymer gels and supercritical extraction (SCE) for making foams starts with an emulsion. An emulsion is basically a suspension of two immiscible liquids such as oil and water. Usually a surfactant is added to stabilize the emulsion and to reduce interfacial tension which reduces the work of forming the emulsion. If the minor constituent is the continuous phase, the suspension is called an inverse emulsion (Fig. 16).

Moreover, when the minor continuous phase is a polymerizable liquid monomer, it becomes a solid polymer during inverse emulsion polymerization. A polymer foam can then be formed by removal of the major phase liquid. We have found that polymerizing a water-in-styrene (oil) inverse emulsion produces a polystyrene foam with uniform open cells after the water is evaporated. The appeal of the inverse emulsion polymerization approach is the independent adjustability of cell size for a given foam density, by choice of surfactant.

A surfactant molecule concentrates at an interface between the oil and water because it is amphipathic, that is, it has polar segments having water affinity and nonpolar segments having oil affinity. Both oil-in-water and water-in-oil emulsions are possible, depending not only on the relative amounts of water and oil but also on the steric nature of the surfactant. For example, due simply to spatial considerations, coupling a bulky nonpolar segment or block will tend to produce an

interface curved toward the water phase, and hence to favor the water-droplet-in-oil emulsion (Fig. 11). The key to this approach for ICF applications is to find by original synthesis a surfactant that forces the major-constituent water phase into droplets of mean diameter one micrometer or less.

Synthesis of the surfactants need to make a water-in-oil emulsion with only 5 to 10 percent oil is a crucial part of the inverse-emulsion foam development process. Fine control of interface curvature (cf. Fig. 11) can be achieved by choice of the monomers that are used to build each of the two blocks, polar and nonpolar, of each surfactant molecule and by varying the length of each block. For efficient surfactant activity, the maximum length of each block has been found to be about 10 monomer units, a short polymer called an oligomer, so that these surfactants are short diblock copolymers, called block co-oligomers. Interface curvature determines the droplet size of the major constituent of the inverse emulsion. Correspondingly, the range of droplet diameters becomes the cell size distribution of the resulting foam.

In research at Case Western Reserve University we have synthesized diblock co-oligomers as surfactant candidates. The system we selected for making block co-oligomers was the 2-substituted oxazolines. These are basic heterocyclic molecule monomers which generate very stable cations as the propagating species.^{2,3,4} They are "living polymers".⁵ That is, one kind of monomer can be added to the initiator and polymerized, then a second kind added and polymerized onto the first to make a block co-oligomer, as shown in Fig. 13.

Typically, about one percent surfactant is used to obtain about a

monolayer at the interfaces, which is optimal for any surfactant. When the block co-oligomer surfactant with $y=61.6$ (cf. Fig. 12) was used to emulsify styrene around water droplets, solid polystyrene foams with the shape of the emulsion container were obtained, with initial concentrations of 30 and 20 wt% styrene. A product which was part solid, part emulsion was obtained with 10 wt% styrene initially. Those solid polymers, when examined by a scanning electron microscope, were found to be derived from stable water-in-oil emulsions. The second surfactant block tested, $y=20.5$, did even better. Here a good water-in-oil emulsion was obtained with only 5% styrene/95% water. The microstructure of the inverse emulsion foam was found to be a squashed soap-bubble morphology, a well-connected and typically very strong geometry, as indicated by the SEM image in Fig. 13. The cell size range is from 5 to 30 μm . By using surfactants with a large nonpolar oligomer block compared to its polar oligomer block, we should be able to force the interface to curve more sharply to produce an even finer cell CH foam.

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FIGURE CAPTIONS

1. Foam cell size vs density for DOE and commercial foams.
2. Cloud points of solutions of high molecular weight polyethylene as a function of concentration. Solutions in alkanes and alkenes fall on upper curve. Solutions in aromatics and hydroaromatics fall on lower curve, 5-10°C less.
3. Polarized optical (160x) and scanning electron (200x) micrographs of dodecane and dodecene gels and foams.
4. Polarized optical (160x) and scanning electron (200x) micrographs of p-xylene and tetralin gels and foams.
5. Crystallization exotherm of ultrahigh molecular weight polyethylene, I.V.=20, at cooling rates of 10, 20, 30 and 60°C/min.
6. Freeze dried polyethylene oxide foam with a density of 50 mg/cm³ is uniform over several centimeters. Cell size is in the range of 2 to 10 µm.
7. The interaction potential in our system has two components. There are Hookean springs between nearest neighbor particles on each chain. All other pairs of particles separated by a distance $r_{i,j}$ interact by a relatively short range inverse power pair potential. It is this second potential which causes the clustering of particles and gelation.

8. The system pictured above has 2500 particles divided between five chains differentiated by colors. We show four states of the system separated by roughly equal intervals of time. Figure (a) shows the initial configuration. Note how the periodic boundary conditions allow the red chain to leave one side of the box and reenter on the other side. Figures (b), (c) and (d) show the time evolution of the system. Note the collapse to a network system of clusters connected by chains.
9. The radial distribution function which measures the average density of particles at radial distances from an average particle is plotted for the configurations shown in Fig. 8. Peak heights which are off-scale are shown. Note particularly the shifts in density to short distances due to cluster formation. The small hump at $r = 14.5$ for the Fig. 8c and 8d configurations may be indicative of the pore size of the sample.
10. With 5-10% oil in water, ordinary emulsions lead to polymer particles, while inverse emulsions can yield polymer foams.
11. Curvature of the liquid-liquid interface can be controlled by adjusting the relative diameter (bulk) of the surfactant's polar and nonpolar oligomer blocks.
12. Synthesis of a diblock co-oligomer surfactant from two oxazoline monomers with polar and nonpolar side groups.
13. Foam made by polymerizing styrene in an inverse aqueous emulsion. Cell size is 5 to 30 μm , and density is 100 mg/cm^3 .

TABLE 1. SOLVENTS USED IN DISSOLUTION AND GELATION OF POLYETHYLENE

<u>Solvent</u>	<u>Formula</u>	<u>Boiling</u>		<u>Density</u>	<u>Solubility</u> <u>parameter</u> (cal/cc) ^{1/2}	<u>H-</u> ^a	^b
		<u>Mol.wt.</u> (g/mol)	<u>Point</u> (°C)			<u>bond</u>	<u>Dissolution</u>
n-Heptane	CH ₃ (CH ₂) ₅ CH ₃	100.2	98.4	0.6837	7.4	P	V
n-Decane	CH ₃ (CH ₂) ₈ CH ₃	142.3	142.3	0.7300	7.7	P	V
n-Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	170.3	216.3	0.7487	7.8	P	V
1-octene	CH ₃ (CH ₂) ₅ CH:CH ₂	112.2	121.3	0.7149	-	P	V
1-dodecene	CH ₃ (CH ₂) ₉ CH:CH ₂	168.3	213.4	0.7584	-	P	V
Decalin	C ₁₀ H ₁₈	138.2	195.6	0.8965	8.8	P	V
Tetralin	C ₁₀ H ₁₂	132.2	205.6	0.9702	9.5	P	V
Naphthalene	C ₁₀ H ₈	128.2	218.	1.0253	-	-	V
Toluene	(C ₆ H ₅)CH ₃	92.2	110.6	0.8669	8.9	P	V
p-xylene	(C ₆ H ₄)(CH ₃) ₂	106.2	138.4	0.8611	8.8	P	V
Ethylbenzene	C ₈ H ₁₀	106.2	136.2	0.8670	-	-	V
Nitrobenzene	(C ₆ H ₅)NO ₂	123.1	210.8	1.2037	-	-	V
Biphenyl	(C ₆ H ₅) ₂	154.2	255.9	0.8660	-	-	V
Diphenylmethane	(C ₆ H ₅) ₂ CH ₂	168.2	264.3	1.0060	-	-	X

^a P=

^b V=

X=

Low density materials

Figure 1

Cloud points of solutions of high-molecular weight polyethylene: effect of solvent and concentration

Gel and foam morphology are effected by solvent - aliphatic compounds

10-05-0285-0677C

Figure 3

Gel and foam morphology are effected by solvent - aromatic compounds

- 31 -

Pure polyethylene crystallizes at progressively lower temperatures as rate of cooling is increased

Irradiated poly(ethylene oxide) gels were freeze dried to produce cellular foams

100 μm

4 μm

- o 5% PEO in water
- o Radiation dose — 15 Mrad (CO^{60} gamma)

Polymer chain condensation model uses spring and van der Waals-like potentials

Five chains of 500 particles evolve to a "fringe micelle"-like structure

Radial polymer-density distribution functions show how structure evolves

An inverse emulsion can be used to prepare a cellular foam

(from Letts et al)

The key to forming stable inverse emulsions is synthesis of proper surfactants. . . .

Steric effects of surfactant control the interface curvature

Typical surfactant structure

10-05-0285-0548

Figure 11

Upon termination the final structure is

where

R_1 is $(\text{CH}_3)_3 \text{C}$ — (less polar - oil affinity)

R_2 is C_2H_5 — (more polar - water affinity)

Figure 12

Figure 13