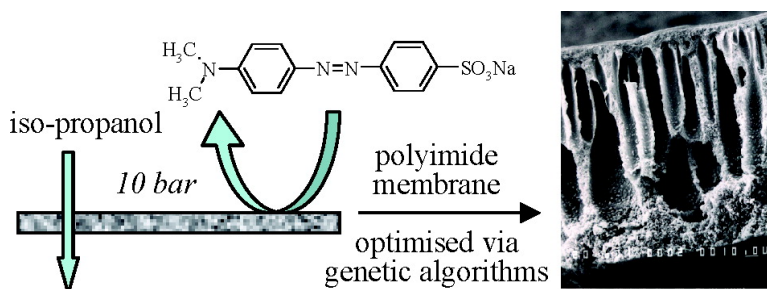


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## Directed Development of High-Performance Membranes via High-Throughput and Combinatorial Strategies

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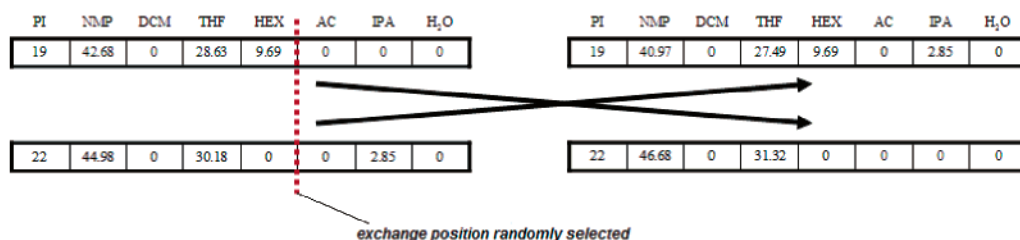
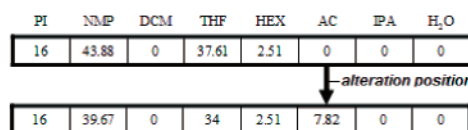
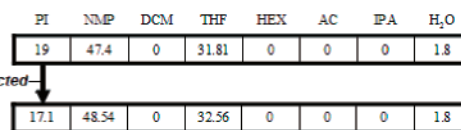
Combinatorial strategies are for the first time applied in membrane technology and prove to be a powerful new tool in the search for novel membrane materials. The selected system for this study is a polyimide solvent-resistant nanofiltration membrane prepared via phase inversion. The phase inversion process is a typical membrane synthesis procedure involving a large number of compositional components, which can each be varied in a wide concentration range. The optimization of the membrane dope composition was performed using evolutionary optimization via genetic algorithms. Compared with the best commercially available membranes, a substantially improved membrane performance could be realized, both on the level of membrane selectivity and on that of permeability. The miniaturized high-throughput synthesis procedure could be scaled up successfully when the polymer dope was sufficiently viscous. It can be anticipated that application of combinatorial techniques can potentially lead to major improvements in all fields of membrane technology, for example water treatment, gas separation, and dialysis, not only on the compositional level but also for instance on the level of membrane synthesis posttreatment and operational conditions.

Membrane technology can offer a sustainable alternative for energy-consuming distillations and waste stream-generating extractions or crystallizations, for example. Even though many industrial-scale membrane plants are currently in operation, a clear need still exists to develop better membranes to open new application areas and solve some remaining problems in the existing processes.<sup>1</sup> To date, the optimization and testing of membranes has been very time-consuming. Because of the many parameters involved in a typical membrane synthesis,<sup>2</sup> an important challenge in developing and optimizing membranes is to find more efficient search strategies to direct membrane composition toward a product with a better separation of the targeted compounds (i.e., higher selectivity combined with useful fluxes). For instance, to prepare a membrane via phase inversion, numerous parameters are involved which can traditionally only be optimized one by one while keeping all others constant. The chance of finding the combined optimum for all these parameters at the same time, and thus preparing the optimal membrane, is very small. For similar types of optimization problems in other fields, design of experiments (DoE) has been introduced to yield the maximum amount of information from a minimum number of experiments.<sup>3–9</sup> A variety of methods has been reported already to realize such design of combinatorial experiments. These include artificial neural networks,<sup>3</sup> statistical approaches,<sup>4</sup> diversity methods,<sup>5</sup> and the use of search strategies, such as genetic algorithms.<sup>6</sup> Despite the successful implementation and revolutionary impact of DoE in the

pharmaceutical industry,<sup>7</sup> material development,<sup>8</sup> and homogeneous and heterogeneous catalysis,<sup>9</sup> no efforts have been reported so far to implement optimization strategies in membrane technology. One of the main reasons was the absence of high-throughput equipment in membrane technology to enable the rapid and accurate collection of large data sets, an essential requirement for the successful implementation of combinatorial strategies. With the authors' very recent development of such a high-throughput testing device for membrane separations, the rapid screening of synthesized membranes with high accuracy became feasible.<sup>10</sup>

This paper presents the first application of DoE, more in particular of evolutionary strategies, to accelerate the development and optimization of membranes. The selected methodology relies on the use of genetic algorithms,<sup>6</sup> based on a biological metaphor of natural evolution, where a gene, fitness, and an environment were translated to membrane composition, permeance/retention combinations, and filtration conditions, respectively. In this work, the preparation of polyimide-based (PI-based) solvent-resistant nanofiltration (SRNF) membranes via phase inversion was selected as case study. Defined as a pressure-driven membrane process working with membranes that show a molecular weight cutoff between 200 and 1000 Da, SRNF has the potential to play an important role in treating the streams generated in chemical processes. Under the commercial name STARMEM, PI-based membranes are currently the state-of-the-art in SRNF, and thus this is the right system to challenge traditional membrane optimization via the parameter-by-parameter approach. The starting point for the study was a classic PI/*N*-methylpyrrolidone (NMP) system with a com-

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**Crossover****Qualitative Mutation****Quantitative Mutation**

**Figure 1.** Illustration of the operators used in the genetic algorithms (see Experimental Section and Supporting Information for more details). The numbers represent the wt % of a given compound in the membrane-casting solution.

position to be optimized by the addition of two volatile solvents (tetrahydrofuran (THF) and dichloromethane (DCM)) and four nonsolvent additives (water, 2-propanol, acetone, and 1-hexanol). This selection was based on literature, where similar combinations of additives resulted in enhanced membrane permeance/retention combinations.<sup>11</sup> The role of volatile solvents in the phase inversion process is to create a dense skin layer. In the case of nonsolvent addition, integrally skinned asymmetric membranes with defect-free skin layers and sublayers devoid of macrovoids are generally formed.<sup>12</sup> An optimized dense skin layer is essential for the retention capacity of the membrane but on the other hand, excessive thickness can lower the permeance drastically.

Crucial in the optimization of consecutive generations of materials is the correct definition of what “fitness” means in natural selection.<sup>6</sup> This fitness allows the prepared membranes to be ranked, and therefore, a so-called “objective function” (O. F.) was defined, formed as a function of membrane retention and permeance. In the search for optimal membranes for the filtration of a dye molecule as a typical probe, genetic principles such as crossover, mutation, and selection of different individuals were applied (Figure 1). The probability for the three operators to happen was set, based on the diversity of the total population of membranes, as indicated by the mean and best value of the membrane performance. Per generation, all polymer solutions, linked to the particular performance of the membrane they produced, were considered simultaneously to allow a parallel search through the multidimensional solution space. This approach already proved to lead rapidly to the synthesis of optimized materials thanks to intelligent search strategies.<sup>13</sup> The studied parameter space of 8 variables would result in about  $9 \times 10^{21}$  possible combinations, which would be impossible to screen in a classical “one-at-a-time” approach.

A total of 192 polymeric solutions were synthesized in the 4 consecutive generations, described below. Table 1 shows the measured performance of the 5 best membranes in each generation, together with three commercial SRNF membranes as reference: two different PI-based membranes and the silicone rubber-based MPF-50 membrane,<sup>14</sup> three of

the most-used commercial reference membranes. The distribution of the calculated O. F. values for all tested membranes is given in Figure 2.

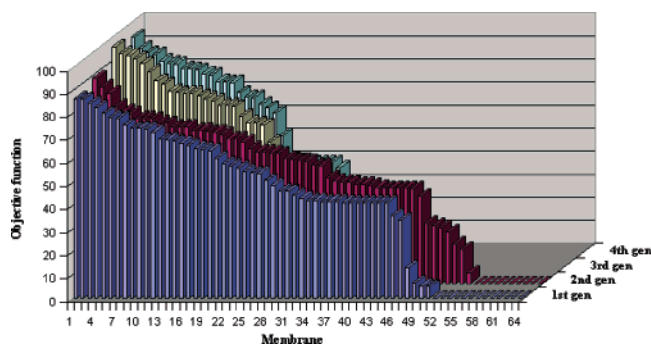
In a first generation, 64 compositions were generated randomly in such a way that each composition contained polyimide, NMP, one volatile cosolvent, and one nonsolvent additive. The selection of the two latter components and their concentration was done randomly within a specified concentration range fixed per class of compounds. Of these 64 randomly generated compositions, 55 actually led to stable polymer solutions from which useful membranes could be cast. The performance of each membrane was translated to an O. F. (see Experimental Section), calculated with a target 2-propanol permeance of 2 L/m<sup>2</sup> h bar and a threshold retention of at least 70%. The permeance target was based on the best results obtained from the commercial reference systems. The selected test solute was Bengal rose (1017.65 Da), for which a 90% rejection would imply that the prepared membrane actually behaves like an SRNF-membrane. However, already in this first generation, a population of 16 membranes showed a total Bengal rose retention. A more ambitious goal thus had to be defined and a much smaller compound, methyl orange (327.33 Da), was chosen for the further membrane optimization. On the basis of the compositions of the first generation (the so-called “parents”) and the new O. F. values calculated from the methyl orange filtrations, the compositions of a second generation were calculated using different genetic operators.

Compared with the first generation, the best performance in the second generation slightly increased (Figure 2). The overall results declined for membranes with an objective function above 72. In contrast, the remaining lower-performing membranes showed a tendency to improve. The procedure thus seemed to be not selective enough, but it also prevented convergence between the best and global optimal membrane too early. To increase the speed of the optimization, only the 32 best-performing membranes of both preceding generations were selected as parents for the third generation. Because the target permeance of 2 L/m<sup>2</sup> h bar was already exceeded by some membranes in the second

**Table 1.** Composition and Performance of the Five Best Membranes for Each Generation

no.	PI <sup>a</sup>	NMP	DCM	THF	HEX	AC	IPA	H <sub>2</sub> O	O. F.	<i>P</i> (L/m <sup>2</sup> h bar) <sup>b</sup>	<i>R</i> (%) <sup>b,c</sup>
generation 1											
1	16.00	43.88	0.00	37.61	2.51	0.00	0.00	0.00	86.39	1.60/0.00	91.25/0.00
2	16.00	42.92	0.00	35.56	5.52	0.00	0.00	0.00	86.27	1.62/0.36	90.95/4.70
3	19.00	47.08	0.00	33.23	0.00	0.69	0.00	0.00	84.65	1.46/0.11	92.77/2.30
4	20.00	52.00	0.00	27.33	0.00	0.67	0.00	0.00	82.71	1.43/0.02	91.99/0.54
5	18.00	47.41	0.00	32.67	0.00	0.00	0.00	1.92	80.20	1.32/0.00	92.58/0.00
generation 2											
1	16.00	47.45	0.00	30.84	5.71	0.00	0.00	0.00	89.08	2.18/0.00	86.61/0.00
2	16.00	40.65	0.00	34.84	2.51	6.00	0.00	0.00	85.31	1.47/0.00	92.98/0.00
3	19.00	48.48	0.00	32.52	0.00	0.00	0.00	0.00	82.47	1.75/0.03	87.49/1.37
4	25.00	27.60	16.91	27.19	3.83	0.00	0.00	0.00	76.80	1.17/0.10	93.60/1.58
5	16.00	26.84	29.40	22.24	5.52	0.00	0.00	0.00	74.70	1.07/0.13	94.88/2.33
generation 3											
1	17.73	47.82	0.00	33.75	0.00	0.69	0.00	0.00	96.32	1.91/0.10	91.99/1.22
2	18.00	48.54	0.00	33.46	0.00	0.00	0.00	0.00	93.38	1.86/0.06	91.91/4.11
3	22.00	50.39	0.00	25.16	0.00	2.46	0.00	0.00	92.47	1.65/0.07	94.22/0.28
4	18.00	45.74	0.00	31.26	0.00	0.00	5.00	0.00	91.28	1.73/0.02	92.02/0.28
5	20.00	45.53	0.00	23.33	8.30	0.00	2.85	0.00	89.05	1.67/0.11	91.64/4.22
generation 4											
1	22.00	51.04	0.00	24.50	0.00	2.46	0.00	0.00	94.15	1.74/0.08	93.50/0.56
2	16.00	43.05	0.00	38.44	2.51	0.00	0.00	0.00	89.73	1.94/0.00	88.86/0.00
3	20.00	46.31	0.00	22.55	8.30	0.00	2.85	0.00	87.46	1.87/0.00	88.41/0.00
4	16.50	43.61	0.00	37.38	2.51	0.00	0.00	0.00	86.69	1.54/0.08	92.49/2.35
5	21.50	50.72	0.00	25.32	0.00	2.46	0.00	0.00	83.84	1.54/0.04	90.85/3.59
reference membranes											
Starmem 120									59.25	0.66/0.02	92.25/1.18
Starmem 240									52.21	0.52/0.06	89.94/1.90
MPF-50									22.15	1.05/0.45	61.10/13.41

<sup>a</sup> The concentrations of polyimide and liquids (HEX = 1-hexanol, AC = acetone, IPA = 2-propanol) are given in wt %. <sup>b</sup> The permeance (*P*) and retention (*R*) are described as average/standard deviation. <sup>c</sup> Analyte adsorption on the membrane could be excluded by mass balances, typically correct within 1%, and by bringing the tested membranes in 50 mL 2-propanol to desorb possibly sorbed dye. Less than 0.5% of the present dye was thus found.



**Figure 2.** Distribution of membrane performance expressed as objective functions over the 4 generations.

generation, this parameter was set at 3 L/m<sup>2</sup> h bar and thus gave a higher weight to permeance in the calculation of the O. F. The O. F. values of all 1st and 2nd generation membranes were recalculated to this target before generating the third generation.

The best performance in the third generation of 32 membranes increased significantly, together with a significant increase in overall performance (O. F.<sub>average</sub>/O. F.<sub>maximal</sub>) from 0.30 and 0.32 to 0.45 over the three generations, and a decrease in population variability (O. F.<sub>best</sub> – O. F.<sub>average</sub>) from 43.35 and 45.73 to 33.37. These are 2 crucial observations to prove that this strategy is leading to a progressive optimization.<sup>13</sup>

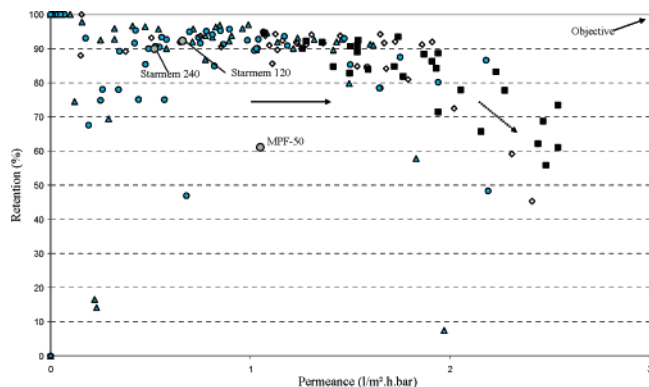
To verify if the assumed optimum was actually also the maximum attainable membrane performance within the

parameter space of experimental filtration conditions, a 4th generation was prepared, in which only quantitative mutations were allowed to take place. This procedure was intended to fine tune the polymer compositions and to avoid jumping out of the optimal parameter space. The objective here was to create more permeable membranes without significant loss of retention and thus to increase the best membrane performance. Therefore, the best membranes of the 3 preceding generations with O. F. values above 80 were selected. In each composition, the concentration of one compound was changed with a small step (2,3 to 10, 0% of the original weight or volume): it was increased for the solvent and decreased for the PI, cosolvent, or nonsolvent concentration.

The testing of this last generation indeed confirmed that the optimum had been reached in the preceding population; most membranes in the 4th generation showed a higher permeance, but retention was decreased (Figure 3), suggesting that the maximum was reached for the given polymer system. The results were thus reflected in lower O. F. values with no significant change in overall performance (0.441) or variability (31.76).

As clearly shown in Figure 3, this high-throughput experiment together with the use of combinatorial strategies defined many different membrane-casting solutions that all led to high-performance membranes, by far superior to the available commercial SRNF membranes. It should be noted that among the almost 200 membranes prepared this way





**Figure 3.** Performances of the 4 generations: ( $\blacktriangle$ ) 1st generation, ( $\circ$ ) 2nd generation, ( $\diamond$ ) 3rd generation, and ( $\blacksquare$ ) 4th generation. The solid arrow indicates the tendency of changing performance from the first/second generation to the third generation. The dashed arrow shows the trend when going from the third to the fourth generation. The target permeance was set at 3 L/m<sup>2</sup> h bar and 100% methyl orange retention.

the membranes that performed badly in the methyl orange rejection in 2-propanol could still be of interest for other separations. For instance, solutions with a PI concentration of more than 22 wt % gave dense membranes with low or no permeance and were thus excluded during the optimization process. These membranes could however be of interest in other solvents that show a high PI affinity and enhanced membrane swelling or for the rejection of still smaller compounds. Preliminary experiments in other solvents also proved an even more drastic outperformance of the prepared membranes with permeances in diethyl ether that were up to six times higher than the commercial membranes at almost total rejection of the (*R,R*)-Cr<sup>III</sup>-Salen catalyst (632,26 Da), a typical catalyst for homogeneous reactions. Crucial in the whole evolutionary approach is the reliability of the measured filtration data in a certain generation which define the direct input for the next generation. The fact that measurements in duplicate and even triplicate could be achieved easily within reasonable time frames was clearly another major advantage of the high-throughput model. In total, the data of the four generations are the result of more than 500 runs collected over a period of less than 2 months.

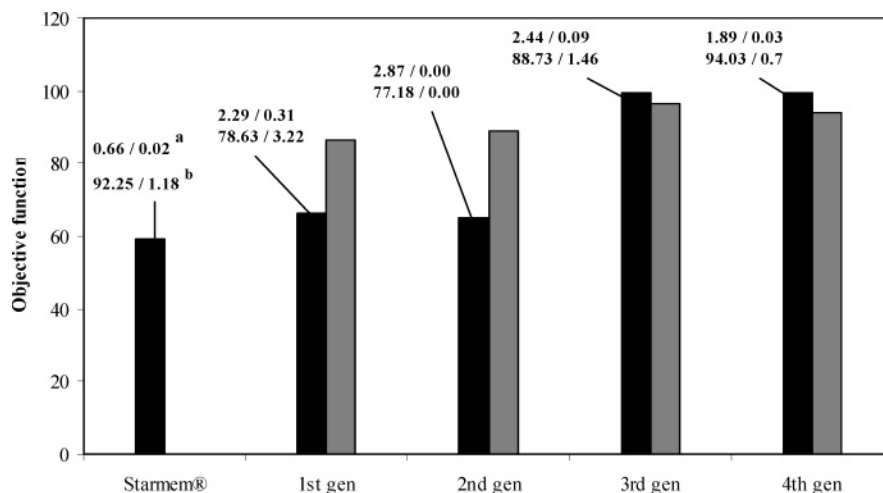
Finally, the best-performing membrane of each generation was scaled up to examine extrapolation of the miniaturized high-throughput synthesis to conventional lab-scale and, possibly later, to industrial scale (Figure 4). In comparison with the high-throughput synthesized membranes, the permeance of the “lab-scale synthesized” membranes was higher and the retention was lower. This was most significant for the best membranes of the first 2 generations, which were cast from polymer solutions with a very low viscosity. For the best membranes of the later generations, cast from more viscous solutions, retention and permeance hardly changed during upscaling, as reflected in the comparable O. F. values.

The combinatorial strategies coupled to high-throughput experimentation led to several high performing membranes with compositions that would never have been found via conventional experimental approaches and with significantly improved separation power compared with industrial state-of-the-art membranes. The coupling of combinatorial strategies to high-throughput testing enabled the directed collection of much data in a short time. The evolutionary procedures were setup in such a way that a high certainty was combined with rapid progression of convergence between the best and optimal membrane performance. A final fine-tuning procedure confirmed the realization of an optimum in three generations. The miniaturized high-throughput membrane synthesis was successfully scaled up to standard lab-scale preparation.

Combinatorial techniques thus clearly offer a practically feasible and very powerful tool for the efficient design of optimized high-performance membranes for all different processes covered in membrane technology, such as gas separation, dialysis, and reverse osmosis. Such an approach should not be limited to compositional optimization but could also, for instance, be applied on the level of membrane synthesis post-treatment and operational conditions.

## Experimental Section

The membranes were synthesized via a phase inversion procedure. The casting solutions were prepared by means of a Tecan RSP 100 automated liquid handler and included the following components in different concentrations (wt



**Figure 4.** Performance of the scaled up (black) and evolutionary optimized (gray) best membranes of each generation. The permeance<sup>a</sup> and retention<sup>b</sup> are given as average/standard deviation.

polyimide (Matrimid 9725 US), NMP as the solvent; THF or DCM as the cosolvent; and 1-hexanol, acetone, 2-propanol, or deionized water as the nonsolvent additive (Table 1). The casting was carried out on a polypropylene/polyethylene support (Vileda nonwoven FO 2471), in parallel for four membranes ( $6 \times 33$  cm each or  $18.2 \times 33$  cm for the scaled up membrane) with a laboratory-made casting device. The solvent was allowed to evaporate for 30 s, after which the film (250  $\mu\text{m}$ ) was immersed in deionized water at room temperature. The membranes were posttreated by solvent-exchange for 3 h in 2-propanol, followed by immersion for 3 days in a toluene/2-methyl-4-pentanone/mineral oil solution with a 40/40/20 volume ratio. Finally, the membrane sheets were dried for 1 h at 60 °C. The MPF-50 and Starmem membranes were obtained respectively from Koch Membrane Systems (Wilmington, USA) and M. E. T. (London, UK).

HT-screening tests were performed with a laboratory-made HT-filtration module, currently commercialized by Agila Belgium, allowing 16 simultaneous filtrations in separate feed cells with controlled stirring.<sup>10</sup> To exclude outliers, 2 or 3 filtration experiments for each membrane were conducted (5 to 6 for the upscaled membranes). A 70  $\mu\text{M}$  methyl orange solution in 2-propanol at room temperature was selected as a typical SRNF feed. A 10 bar nitrogen pressure was applied on all cells and feeds (0.030 L) were stirred mechanically.

The permeance ( $P$ ) is expressed in  $\text{L}/\text{m}^2 \text{ h bar}$ , while retention ( $R$ ) is defined as  $(1 - C_p/C_f) \times 100$  with  $C_p$  being the measured dye concentration in the permeates and  $C_f$  being the initial dye concentration in the feed. The UV-vis measurements were recorded on a Perkin-Elmer Lambda 12 UV-vis spectrophotometer at 413 nm.

To obtain the objective function, both measured results were first converted to coordinates between 0 and 100 by the operation

$$C_1 = (P_{\text{measured}}/P_{\text{target}}) \times 100$$

$$C_2 = ((R_{\text{measured}} - R_{\text{threshold}})/(100 - R_{\text{threshold}})) \times 100$$

(if the solution for  $C_2$  had a negative sign, it was given a value of zero).

Target permeance and threshold retention were chosen to adjust the weight of both components in the objective function. The O. F. is determined by the subtraction of the distance  $(0, 0) - (100, 100)$  with  $(C_1, C_2) - (100, 100)$  in the coordinate space. Thermodynamically unstable polymer solutions and defect membranes were given a zero value.

The successive generations during the evolutionary optimization were generated by applying the operators' mutation and crossover. Parent compositions were selected for fitness proportionally on the basis of the O. F. value (fittest membranes) via the wheel roulette method<sup>8a</sup> and then adapted by crossover and quantitative mutation. For the latter, magnitude and direction (increased or decreased amounts) of change to prepare a new composition were chosen critically per case, on the basis of the general principles of phase inversion. Random selection among the whole generation occurred for qualitative mutation. The exchange and alteration positions in the case of crossover and mutations, respectively, were determined randomly.

The probabilities for applying the evolutionary operators were changed during the optimization in a self-adapting way (as described in ref 8a, page 152). The control parameters A and B were fixed at 0.5. After adaptation via the operators, compositions were normalized to 100% by recalculating the compositions of the solvents and cosolvents, while leaving the composition of nonsolvents unchanged.

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**Supporting Information Available.** Tables showing the production of the first, second, third, and fourth generations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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