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# Formation of rigid polyurethane foams with semi-fluorinated diblock copolymeric surfactants

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Semi-fluorinated diblock copolymers were employed as surfactants in the formation of water-blown closed cell rigid polyurethane foams by the 'tube'-foam method. These fluorosurfactants consisted of a poly(methyl methacrylate) block and a poly[(1H,1H,2H,2H-perfluoroalkyl) methacrylate] block in which the perfluoroalkyl groups were either butyl or hexyl. As references, model foams were prepared with commercially applied siloxane surfactant, inert silica, and no surfactant. Foams based on the fluorosurfactants contained many small cells while the others showed larger and markedly more irregular cells. Scanning electron microscopy (SEM) and the average foam height (AFH) were used for characterization. SEM revealed that foam cell diameters as small as 100 $\mu$m could be realized when using fluorosurfactants in contrast to very large cell sizes and irregular shapes when a commercially available siloxane surfactant, an inert inorganic solid, or no surfactant at all were used. Furthermore, relatively large AFH-values were observed when only a semi-fluorinated diblock copolymer was used. However, the combination of siloxane surfactant with a fluorine-containing surfactant resulted in unparalleled high AFHs. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Polyurethane (PU) foams can be divided into different groups according to their physical properties. Their field of application is determined by two important parameters: (i) the density, and (ii) the rigidity of the PU material. In order of increasing foam density: low density foams (flexibles and rigids), medium density microcellular foams (usually semi-rigid) and solid thermoplastic polyurethanes (TPUs) are discerned. The type of foam of interest for this publication is characterized by a low density in combination with a high rigidity. These rigid closed-cell PU foams exhibit outstanding thermal insulation properties which make them excellent materials for refrigerator insulation[1,2].

Cellular polyurethanes are manufactured by using blowing agents. Until recently, chlorofluorocarbons (CFCs) were applied in the production of rigid foams, i.e. trichloromonofluoromethane (CFC-11), sometimes mixed with dichlorodifluoromethane (CFM-12), and dichloromethane[3]. The main advantage of CFC-11 is the low thermal conductivity of the CFC-11 vapour which is retained in the closed-cell rigid foam leading to unparalleled insulating properties.

Currently the use of CFCs is prohibited because of its ozone depletion potential (ODP)[4]. In addition to low ODP, possible substitutes should also possess a neglectable global warming potential (GWP). Replacements for CFCs as blowing agents are pentane and carbon dioxide which have a zero ODP and a very small GWP. The latter is less

hazardous and easier to handle. Although $CO_2$-foams are prone to gas-leakage[5], a recent study has shown that these foams can be employed as insulation material for refrigerators[6].
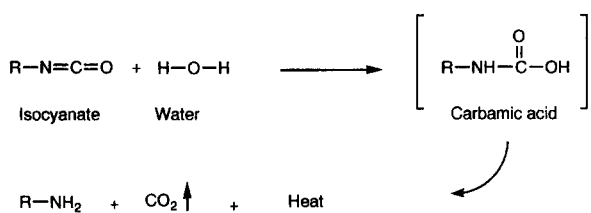
It is known that thermal conductivity in rigid PU foams changes with cell size[7]. Hence, this dependence can be used to overcome the high thermal conductivity of carbon dioxide, which is about twice as large as for CFC-11. By reducing the cell size of rigid PU foams the isolating capacity can be significantly enhanced.

The most convenient way of introducing carbon dioxide in PU foams is by the reaction of isocyanates with water (*Scheme 1*)[8]. The intermediate product, a carbamic acid, is unstable and spontaneously decomposes to a primary amine and carbon dioxide. These type of PU foams are designated as water blown. The amine immediately takes place in a further reaction with isocyanate to give a disubstituted urea (*Scheme 2*).

For the production of PU foams the use of surfactants is essential. Their action during the foam formation process is manifold: (i) stabilizing the dispersion of any immiscible reaction components; (ii) promoting nucleation of bubbles during mixing; (iii) stabilizing gas bubbles in the rising foam; and (iv) preventing the foam from collapsing by reducing stress concentrations until the ongoing polymerization reaction has given it sufficient mechanical strength.

The first known surfactants for conventional foam processes were organic non-ionic such as nonyl phenol ethoxylates[9], fatty acid ethoxylates and alkylene oxide block copolymers[3]. Later, poly(dialkyl siloxanes) became

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R—N=C=O + H—O—H $\longrightarrow$ $\left[ \begin{array}{c} O \\ \parallel \\ R-NH-C-OH \end{array} \right]$

Isocyanate    Water            Carbamic acid

R—NH$_2$ + CO$_2$↑ + Heat $\longleftarrow$

**Scheme 1**

R—NH$_2$ + R'—N=C=O $\longrightarrow$ $\begin{array}{c} O \\ \parallel \\ R-NH-C-NH-R' \end{array}$

Amine    Isocyanate           Disubstituted urea

**Scheme 2**

widely used. Nowadays, graft copolymers are applied which consist of an inorganic polysiloxane backbone with polyether side chains[10]. The effectiveness of poly(oxyalkylene) grafted polysiloxane surfactants depends strongly on the length of the polysiloxane backbone and on the number, length and composition of the grafts.

For the development of foam processes involving carbon dioxide it is necessary to elaborate new surfactants which are adapted to these new polyurethane foam systems. It is known that fluorinated materials exhibit good solubility in liquid and supercritical carbon dioxide and are so-called $CO_2$-philic[11-16]. Recently, the use of fluorinated blowing agents in the preparation of PU foams was reported[17,18]. The action of so-called low boiling blowing agents (LBBAs) is based on two main aspects: (i) solubility of the LBBA in the reaction mixture, and (ii) the nucleation behaviour[19]. This theory predicts good nucleation if insoluble droplets are present from which expansion starts. Other attempts mention the use of fluorinated inert, insoluble, non-blowing liquids[20,21]. Both methods are based on an improved nucleation process.

In addition, fluorinated surfactants are mentioned in patent literature. They are all used in combination with carbon dioxide as blowing gas and fluorocarbon (FC) non-soluble blowing agents[22-24]. The fluorosurfactants provide proper dispersion of the FCs. One type of surfactant of low molecular weight consists of ω-perfluoroalkyl-1-alkanols, where the perfluoro segment is either coupled directly to the hydrocarbon segment or via a sulfone amide group[22]. Macromolecular surfactants with a small partially or perfluorinated group and a lyophilic block constituted of propene oxide units up to a degree of polymerization of 70 are also known to be applicable[23]. Furthermore, the use of an oligomeric acrylate containing polyoxyalkylene and fluoroalkyl side chains has been reported[24].

In this report semi-fluorinated diblock copolymers are presented as a new type of polymeric surfactants in the preparation of low density rigid PU foams used without additional FC blowing agents. Foams were prepared in small laboratory scale test tubes. This 'tube'-foam method allowed a feasible way to gain qualitative information on the performance of semi-fluorinated diblock copolymeric surfactants. Two different diblock copolymers have been tested, one with a high overall molecular weight and perfluorohexyl side chains, and one with a shorter length and perfluorobutyl side chains. The results with respect to morphology, cell size and average height of the obtained

foams are discussed and compared to a commercially applied polysiloxane surfactant.

## EXPERIMENTAL

### Materials

Polyol mixture and polymeric diphenylmethane diisocyanate (PMDI) Voranate M220 (DOW Chemical Company®) were DOW products and used without further purifications. Dimethylcyclohexyl amine (DSM), Niax A-1 (70% bis(dimethylamino ethyl ether) and 30% dipropylene glycol) (Union Carbide), Curethane 206 (Dow) were used as catalysts. Demineralized water was used throughout. A commercially available siloxane L-6900 (OSi Specialties), talc powder and several semi-fluorinated diblock copolymers[25,26] were used as surfactant.

### Synthesis of polyurethane foams

All experiments were carried out in a climatized room at 18°C. Test tubes with an internal diameter $\varnothing_i \approx 11.0$ mm, an outer diameter $\varnothing_o = 12.5$ mm and a length $l = 120.0$ mm were filled with surfactant expressed in parts per one hundred parts of polyol (pphp). Then, the desired amount of polyol/catalysts mixture was added via a syringe and shaken for 2 min with a ROFA-MAVI tehtnica EV-204 shaking device at 2500 rpm. The PMDI added via a syringe was weighed into the test tube and the resulting mixture was immediately thoroughly shaken for a designated period. The occurrence of an exothermic reaction was observed by a large volume and temperature increase. Foams containing semi-fluorinated surfactant had a yellowish colour. Foams based on silicone surfactant alone had a light brown appearance. Foams with inert silica powder or no surfactant collapsed and were brown coloured.

### Scanning electron microscopy (SEM)

SEM was performed on a Zeiss DSM 962 scanning electron microscope. Samples were cut in either radial or axial direction and fixed on a metal sample holder by using carbon-based glue. After drying overnight at 40°C the samples were subjected to a coating procedure. A Bulzers Union MED 010 sputtering apparatus (vacuum < 0.05 mbar) was used in order to deposit a 20 nm thick gold/palladium layer on the sample.
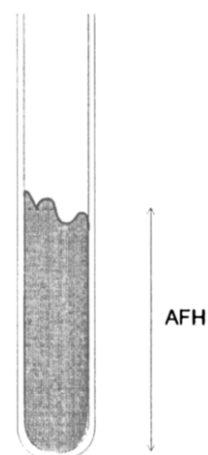


**Figure 1** Schematic representation of the definition of average foam height (AFH).

AFHs were determined by triplicate measurement of the estimated average foam heights with a marking gauge and taking the average value. *Figure 1* depicts the value defined as AFH.

## RESULTS AND DISCUSSION

### Foam preparation

Small-scale laboratory experiments were performed in order to study the performance of semi-fluorinated diblock copolymers as surfactants for the preparation of rigid closed-cell PU foams. The experimental procedure is diagrammatically depicted in *Scheme 3*.

First, the polyol/catalysts-surfactant mixture was shaken for a certain time, $t_1$. In the second step the PMDI was added and the two-phase system was mixed thoroughly for a period referred to as the mixing time, $t_m$. Subsequently, the exothermic polyurethane formation took place which was accompanied by a large volume expansion and a temperature rise of several tens of degrees.

In general, bulk foams are self-insulating and show almost adiabatic conditions. The 'tube'-foam is made under high heat-loss conditions. Surfactants for PU foams influence the foam structure until the maximum foam dimensions have been reached. Cell size is determined in the initial nucelation state. During rise of the foam, the surfactant acts as a foam stabilizer. Even in bulk foams, the temperature is still increasing and considerably lower than the maximum temperature before the maximum foam dimensions have been reached. In other words, the performance of surfactants is most important in the low temperature region, in bulk foams as well as in the described 'tube'-foam[7]. Therefore, the performance of surfactants is not to be expected to be much different under the conditions described here.

The fluorosurfactants used were poly(methyl methacrylate-*block*-(1H,1H,2H,2H perfluorohexyl) methacrylate) (P(MMA-b-F4H2MA)-1.5) and poly(methyl methacrylate-*block*-(1H, 1H,2H,2H-perfluorooctyl) methacrylate) (P(MMA-b-F6H2MA)-5) (*Scheme 1*)[25,26]. The degrees of polymerization, *DP*, of the consecutive blocks of the semi-fluorinated diblock copolymers are listed in *Table 1*. Both polymers had a narrow molecular weight distribution and were well defined. Although both were asymmetric, P(MMA-b-F6H2MA)-5 contained relatively the largest amount of fluorine. In addition to the fluorinated surfactants a commercially available siloxane surfactant was tested as a reference. Because the semi-fluorinated diblock copolymers appeared to be poorly soluble in the polyol/catalysts mixture
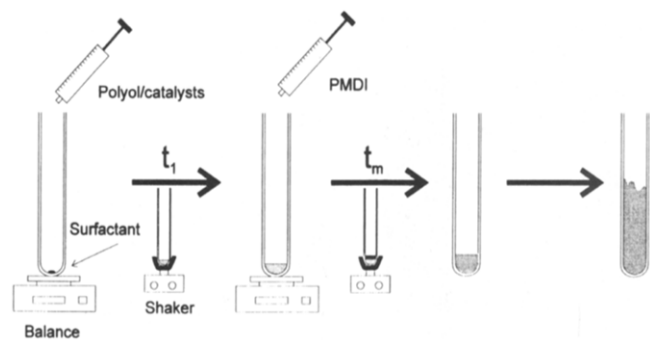
**Table 1** Degree of polymerization of the consecutive PMMA and PFnH2MA blocks and polydispersity of the PMMA block of semi-fluorinated diblock copolymers

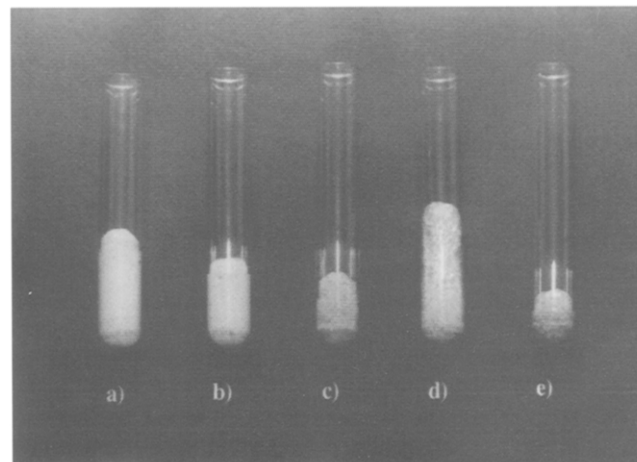| Surfactant | $DP_{PMMA}$ | $DP_{PFnH2MA}$ | Polydispersity$_{PMMA}$ |
|---|---|---|---|
| P(MMA-b-F4H2MA)-1.5 | 104 | 33 | 1.20 |
| P(MMA-b-F6H2MA)-5 | 47 | 24 | 1.13 |



**Figure 2** Photographs of polyurethane foams which visualize the effect of addition of 2.0 pphp of different surfactants: (a) P(MMA-b-F4H2MA)-1.4; (b) P(MMA-b-F6H2MA)-5; (c) talc powder; (d) siloxane; and (e) no surfactant at all. Mixing time = 20 s.

and in the PMDI as well, some small solid particles remained in the foam. Allowing the surfactant to dissolve in the polyol/ catalysts mixture overnight or stirring for a much longer time did not improve the quality of the resulting foams. To investigate the influence of the presence of solid substances a series of experiments was performed in which talc powder $(Mg_3(OH)_2[Si_2O_5]_2)$ was added. *Figure 2* demonstrates striking differences between foams which were prepared with various additives. Foams with semi-fluorinated diblock copolymers as surfactant are shown in *Figure 2*(a) and (b).

Cells looked mostly closed and narrowly distributed in size. The diblock copolymer with the perfluorobutyl side chains and the lowest molecular weight displayed a larger volume expansion than the foam with the other diblock copolymer as surfactant. Foams prepared with talc powder, siloxane surfactant and no surfactant, represented by *Figure 2*(c), (d) and (e), respectively, had markedly more irregular cells and the foam structure partly even collapsed in the case of the talc foam and the foam in which no surfactant was added [*Figure 2*(c) and (e)]. The height of the foam with the siloxane surfactant [*Figure 2*(d)] is, though irregular, largest of all prepared foams.

### Morphology

In *Figure 3*(a) and (b) scanning electron micrographs are shown of PU foams with 0.5 parts per one hundred parts of polyol (pphp) and 2.0 pphp of P(MMA-b-F6H2MA)-5, respectively. The slices shown were cut in radial direction. It could be seen that the cells were not uniform, i.e. large variations in size and shape existed. A scanning electron micrograph of a PU foam containing 2.0 pphp of P(MMA-b-F4H2MA)-1.5 is depicted in *Figure 3*(c). This micrograph was taken from a piece of PU material which was cut in the axial direction. Typical for the axial slices, no unusual anisotropic structures were detectable. For both diblock copolymers the minimum cell size was about 100 μm. No
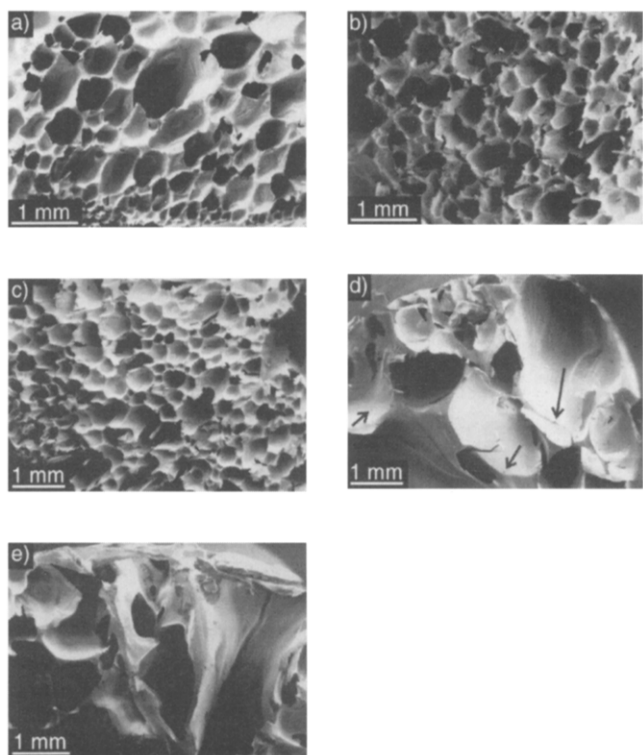


**Scheme 3**

**Figure 3** Scanning electron micrographs of PU foams with (a) 0.5 pphp of P(MMA-b-F6H2MA)-5; (b) 2.0 pphp of P(MMA-b-F6H2MA)-5; (c) 2.0 pphp of P(MMA-b-F4H2MA)-1.4; (d) 2.0 pphp of talc powder; and (e) no surfactant at all.
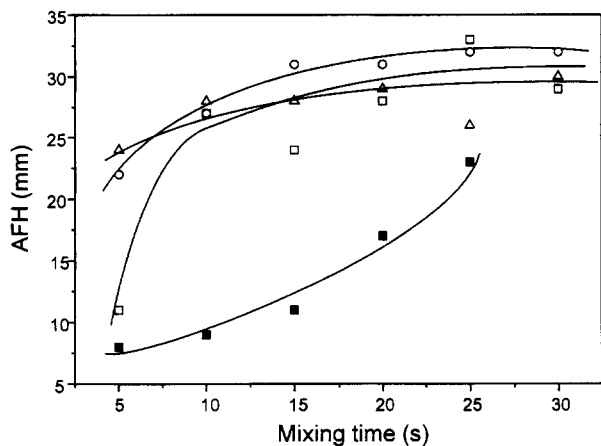


**Figure 4** Average foam height (AFH) as a function of mixing time for (□) 0.1 pphp of P(MMA-b-F6H2MA)-5, (O) 0.5 pphp of P(MMA-b-F6H2MA)-5, (△) 2.0 pphp of P(MMA-b-F6H2MA)-5, and (■) no surfactant at all.

significant dependence on the surfactant concentration was found.

When 2.0 pphp of talc powder were used instead of the diblock copolymeric surfactant [*Figure 3*(d)] very large, irregular cells and many broken cell walls were observed. Solid particles could be seen inside the foam on the walls of the cells as indicated by the arrows. The same undefined large cell structures as for the foams with the talc were obtained when no surfactant was used at all [*Figure 3*(e)].

*Foam heights*

Average foam heights (AFHs) as a function of different process parameters can give a semi-quantitative measure for the effectiveness of the employed surfactant.
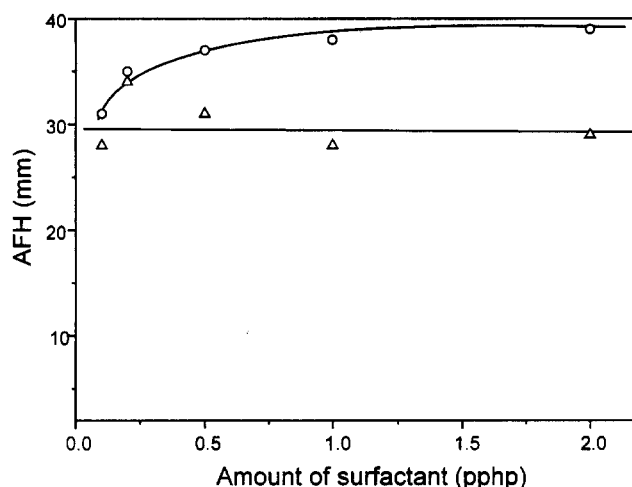


**Figure 5** Average foam height (AFH) as a function of the amount of added semi-fluorinated diblock copolymer where (O) is P(MMA-b-F4H2MA)-1.4 and (△) is P(MMA-b-F6H2MA)-5. Mixing time = 20 s.
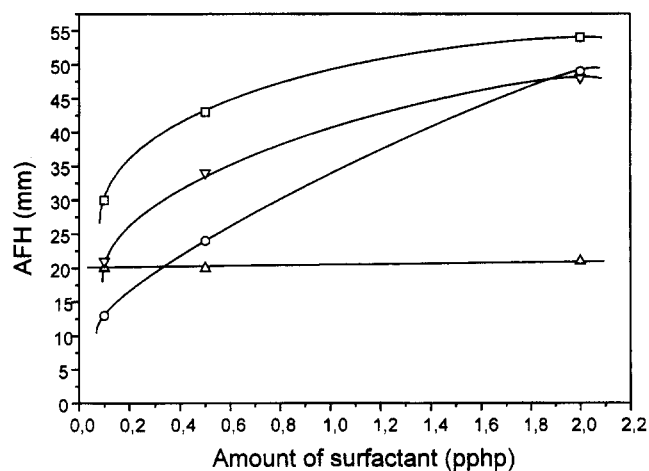


**Figure 6** Average foam height as a function of the amount of added surfactant where (▽) is siloxane, (□) is siloxane + 0.1 pphp of P(MMA-b-F6H2MA)-5, (O) is siloxane + 0.1 pphp of talc, and (△) is talc. Mixing time = 20 s.

First, the AFH was measured as a function of mixing time for foams containing, respectively, 0.1, 0.5 and 2.0 pphp of P(MMA-b-F6H2MA)-5 and no surfactant at all (*Figure 4*). In all cases AFHs increased with increasing mixing time probably because the used polyol mixture and the PMDI are not miscible which was indicated by the occurrence of a turbid reaction mixture. Moreover, the evolvement of a good foam depends on the dispersion of the PMDI phase in the polyol/catalyst phase[27]. For constant mixing times markedly higher AFH-values were found when a semi-fluorinated diblock copolymer was added. Differences in AFH upon varying amounts of surfactant were particularly significant at low mixing times yielding an increased AFH with increasing surfactant concentration.

*Figure 5* depicts the AFHs as a function of the amount of added surfactant for both semi-fluorinated diblock copolymers. The diblock copolymer with the perfluorobutyl side groups performed better than the one with the perfluorohexyl side groups, especially at a higher copolymer content. This might be explained by the lower molecular weight of the former which leads to better solubility and faster diffusion from the bulk of the PU reaction mixture to the gas–liquid interfaces around the gas bubbles.

Typically, the fluorosurfactants were highly effective already at low surfactant contents. For amounts higher than *ca.* 0.5 pphp of surfactant, AFHs remained more or less constant at a maximum value.

For comparison, a commercially available siloxane surfactant was used in combination with P(MMA-b-F6H2MA)-5, and in combination with talc powder. Particularly at lower surfactant contents the significant differences in AFH-value reflected different performances (*Figure 6*). The combination of siloxalie with semi-fluorinated diblock copolymer yielded the highest AFH-values over the entire range of surfactant concentration. At higher contents of siloxane surfactant the relative amount of added second component, i.e. fluorosurfactant or talc, decreased and the differences in AFH diminished. Adding talc powder without surfactant resulted in a constant AFH unaffected by the amount of talc. In addition, it must be taken into consideration that the foams with the talc powder and with no surfactant collapsed during the exothermic foam formation reaction.

## CONCLUSIONS

Semi-fluorinated diblock copolymers based on methyl methacrylate and (1H,1H,2H,2H perfluoroalkyl) methacrylate were used as surfactants for the formation of water-blown polyurethane foams. However, the observed poor solubility of this type of surfactants in both the polyol/catalysts mixture as well as in the polymeric diphenylmethane diisocyanate might affect foam structure.

Recently published theory predicts increased nucleation capacity with decreased solubility[7,19]. These effects have been confirmed in practice by normal and low boiling per- and partially fluorinated blowing agents. Considering the poor solubility of the macromolecular fluorosurfactants it can be hypothesized that this might result in a nucleation promoting effect, similar to the action of LBBAs. This is supported by the observation that smaller cell sizes have been observed in these cases. As cell size is proportional to the number of nucleation points the obtained small cells might arise from many nucleation points given by the unsolubilized fluorosurfactant.

However, another important point demands attention. It is known that semi-fluorinated diblock copolymers form micelles in selective solvents[26,28]. Micelle formation occurs already at very low concentrations (*ca.* 0.01 wt% in toluene[26,28]) which is a good solvent for the PMMA block. These micelles might also be formed during the PU foam formation where the core of the micelle consists of the fluorinated block shielded by the PMMA block in the shell. Hence, the occurrence of micelles favours nucleation and leads to an increased number of cells.

The stabilizing power of any surfactant is only available in solution. Thus, the small amount of dissolved fluorosurfactant still appeared to be very effective in the stabilization of the rising foam. Comparative experiments in which inert talc powder was used as a solid impurity in order to mimic the insoluble fluorine containing surfactant indicated that a certain amount of fluorosurfactant was dissolved in the polyol-PMDI dispersion.

Although the 'tube'-foam method cannot be directly compared to the larger scale cup experiments, some basic features evolved of the use of semi-fluorinated diblock copolymers as surfactant. It can be postulated that the action of the fluorine containing surfactants might originate from a very useful promoting of nucleation of small bubbles and successive stabilization of the these bubbles.

The largest average foam heights were obtained when a commercial siloxane surfactant was applied. Combination of the siloxane surfactant with the diblock copolymer with the perfluorobutyl side chains led to unparalleled high average foam heights. This might originate from an improved nucleation caused by the fluorosurfactant, while the siloxane surfactant took place in the actual stabilization of the rising foam.

Concerning the cell size, the semi-fluorinated diblock copolymers performed best giving small cells with minimal diameters of *ca.* 100 $\mu$m. The foams in which either talc powder or no surfactant at all was used could not be stabilized and collapsed.

## ACKNOWLEDGEMENTS

## REFERENCES

1.  Kaplan, W. A. and Tabor, R. L., *Cellular Polymers*, 1993, **12**, 102.
2.  Grünbauer, H. J. M. and Folmer, J. C. W., *Journal of Applied Polymer Science*, 1994, **54**, 935.
3.  Woods, G., in *The ICI Polyurethane Book*. ICI Polyurethanes–Wiley, Chicester, 1987.
4.  Banks, R. E., *Journal of Fluorine Chemistry*, 1994, **67**, 193. (and references cited therein).
5.  Haworth, G. J., Srikanth, R. and Fine, H. A., in *Proceedings of the 44th Annual International Appliance Technical Conference*, 1993, p. 1.
6.  Grünbauer, H. J. M., Cikut, L., Hawworth, G. J. and Beerwart, A., *Proceedings of Polyurethanes 1995, SPI Conference*, Chicago, IL, 1995, p. 436.
7.  Grünbauer, H. J. M., in *Polymeric Materials Encyclopedia*, ed. J. Jc. Salamone, Vol. 10. CRC Press, Boca Raton, FL, 1996, p. 7504 e.f.
8.  Grünbauer, H. J. M., Thoen, J. A., Folmer, J. C. W. and van Lieshout, H. C., *Cell Plasticity*, 1992, **28**, 37.
9.  Porter, M. R. in *Handbook of Surfactants*, 2nd Ed. Blackie, London, 1994.
10. Koster, J. B., Processing seminar 'rigid foams' on *The International Polyurethane Industry Exhibition and Conference: Utech 92*, The Hague, The Netherlands, 1992.
11. DeSimone, J. M., Guan, Z. and Elsbernd, C. S., *Science*, 1992, **257**, 945.
12. Guan, Z., Combes, J. R., Mencologlu, Y. Z. and DeSimone, J. M., *Macromolecules*, 1993, **26**, 2663.
13. Combes, J. R., Guan, Z. and DeSimone, J. M., *Macromolecules*, 1994, **27**, 865.
14. Guan, Z. and DeSimone, J. M., *Macromolecules*, 1994, **27**, 5527.
15. Consani, K. A. and Smith, R. D., *Journal of Supercritical Fluids*, 1990, **3**, 51.
16. Hoefling, T., Stofesky, D., Reid, M., Beckman, E. and Enick, R. M., *Journal of Supercritical Fluids*, 1992, **5**, 237.
17. Doerge, H. P., Sutej, J. M., Ball, E. E. and Szabat, J. F., US Patent US 5, 397, 808, 14 March, 1995.
18. Wenning, U. and Brodsky, J., European Patent Application EP 405, 439, 1989.
19. De Vos, R., U.S. Patent US 5, 391, 584, 21 February, 1995.
20. Nakamoto, H. and Amayoshi, T., Japanese Patent JP 07 26055, 27 January, 1995.
21. De Vos, R., Thorpe, D. and van Essche, G., European Patent Application EP 605, 105 A1, 1993.
22. Volkert, O. and Hinz, W., US Patent 5, 126, 3 79, 1992.
23. Volkert, O., US Patent 4, 972, 002, 1990.
24. Krupers, M. J., Cabelo, F. M. E. and Möller, M., *Macromolecules Symposium*, 1996, **102**, 99.
25. Krupers, M. J. and Möller, M., *Macromolecular Chemistry and Physics*, 1997, **198**, 2163.
26. Grünbauer, H. J. M., in *Cellular Polymers*, ed. J. M. Burst. Rapra Technology, Shawbury, 1995, p. 366 e.f.
27. Schmidt, D. L., Clarke, D. H. and Urchick, D., *Journal of Cellular Plasticity*, 1984, **20**, 220.
28. Krupers, M. J., Sheiko, S., Möller, M., in preparation.