Polymer synthesis and processing using supercritical carbon dioxide

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Carbon dioxide is a clean and versatile solvent for the synthesis and processing of a range of materials. This review focuses on recent advances in polymer synthesis and processing using liquid and supercritical CO_2. The synthetic techniques discussed include homogeneous solution polymerisation, precipitation polymerisation, dispersion and emulsion polymerisation, and bulk polycondensation. The formation of porous polymers and polymer blends is also considered, and the specific advantages of CO_2 in these processes are evaluated in each case. The use of CO_2 as a solvent for polymer processing is reviewed from a materials perspective, with particular attention being given to the formation of polymers with well defined morphologies. The variable solvent strength associated with supercritical fluids has been utilised in areas such as polymer fractionation and polymer extraction. Plasticisation phenomena have been exploited for the impregnation and heterogeneous chemical modification of polymeric materials. The formation of microcellular polymer foams by pressure induced phase separation is considered, as is the use of CO_2 for polymer particle formation, spray coating, and microlithography. The aim of the review is to highlight the wide range of opportunities available to the materials chemist through the use of carbon dioxide as an alternative solvent.

1 Introduction

The uses of supercritical carbon dioxide as a medium for polymer synthesis[1] and for polymer processing[2] are two interrelated research areas which have attracted much attention recently. The unique physical properties associated with supercritical fluids[3] give rise to a range of intriguing possibilities for the materials chemist, not only in polymer science but also in areas such as organic synthesis,[4] hetero-geneous[5] and homogeneous[6] catalysis, and inorganic/metal–organic coordination chemistry.[7] In the case of supercritical carbon dioxide (scCO_2) there are chemical, environmental, and economic advantages which might be gained from its use as a solvent. On the other hand, the use of supercritical fluids requires elevated pressures and relatively specialised equipment, and these considerations must be balanced carefully with the perceived advantages for a given application. The aim of this article is to review, from a materials chemistry standpoint, recent advances in the use of scCO_2 for the synthesis and processing of polymers. At the same time, a critical assessment will be made of the advantages of this technology in comparison with more established methods. Special emphasis will be given to techniques that make use of the physical and chemical properties of carbon dioxide in order to produce novel polymeric materials.

1.1 Supercritical fluids

A supercritical fluid (SCF) may be defined as a substance for which both temperature and pressure are above the critical values (Fig. 1, Table 1). However, this definition is of limited use since it gives no information about the density of the substance. Darr and Poliakoff offer a more practical defini-tion,[7a] whereby a supercritical fluid is described as "any substance, the temperature and pressure of which are higher than their critical values, and which has a density close to or higher than its critical density". With some exceptions, most applications reviewed here involve CO_2 under conditions of temperature and pressure such that the density frequently exceeds the critical density (0.47 g cm^{-3}). Indeed, many techniques require densities that are in the range expected for conventional liquid solvents ($0.8–1.0 \text{ g cm}^{-3}$). Close to the critical density, SCFs display properties that are to some extent intermediate between those of a liquid and a gas.[3,8,9] For example, a SCF may be relatively dense and dissolve certain solids while being miscible with permanent gases and exhibiting high diffusivity and low viscosity. In addition, supercritical fluids are highly compressible and the density (and therefore solvent properties) can be "tuned" over a wide range by varying pressure [Fig. 2(a)]. This property may be exploited, for example, in the separation of reaction products or in the fractionation of polymers by density programming (Sec-tion 3.1). A large number of the applications described in this review exploit at least one of the unique properties of SCFs, but it should be noted that supercritical conditions might also be employed for more prosaic reasons. For example, many chemical reactions occur well above the critical temperature of CO_2 (31.1 °C). This may necessitate supercritical conditions in order to achieve reasonable solvent densities, irrespective of
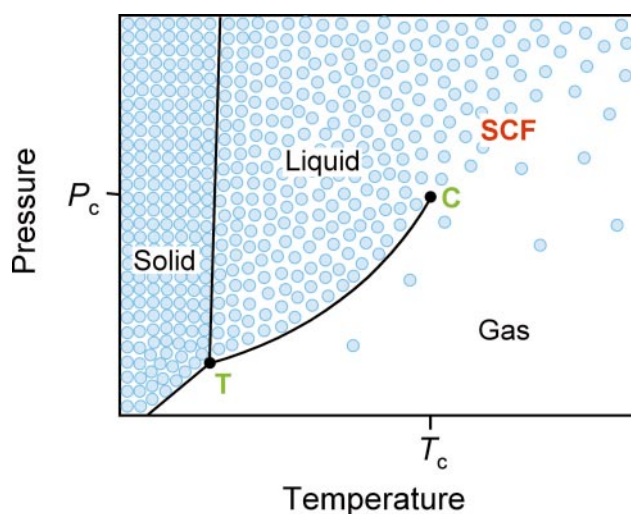

Fig. 1 Schematic pressure–temperature phase diagram for a pure component showing the supercritical fluid (SCF) region (adapted from ref. 7b). The triple point (T) and critical point (C) are marked. The blue circles represent the variation in density of the substance in the different regions of the phase diagram. Note that the density varies continuously between the liquid state and the gas state, providing that the liquid–gas equilibrium line (T–C) is not crossed.

Table 1 Critical parameters for selected substances, taken from refs. 3 and 7(a). T_c=critical temperature, P_c=critical pressure, ρ_c=critical density (*i.e.*, the density at the critical pressure and critical temperature). Dielectric constant of CO_2=1.01–1.67 (ref. 13); polarisability, α, of CO_2=27.5×10^{-25} cm^3 (ref. 14); dipole moment, μ, of CO_2=0.0 D

Substance	T_c/°C	P_c/bar	ρ_c/g cm^{-3}
CH_4	−82.5	46.4	0.16
C_2H_4	10.0	51.2	0.22
C_2F_6	19.9	30.6	0.62
CHF_3	26.2	48.5	0.62
$CClF_3$	28.9	38.6	0.58
CO_2	**31.1**	**73.8**	**0.47**
C_2H_6	32.4	48.8	0.20
SF_6	45.6	37.2	0.73
Propylene	91.9	46.1	0.24
Propane	97.2	42.5	0.22
NH_3	132.5	112.8	0.24
Pentane	187.1	33.7	0.23
^{i}PrOH	235.4	47.6	0.27
MeOH	240.6	79.9	0.27
EtOH	243.5	63.8	0.28
^{i}BuOH	275.1	43.0	0.27
Benzene	289.0	48.9	0.30
Pyridine	347.1	56.3	0.31
H_2O	374.2	220.5	0.32

Fig. 2 (a) Graph showing the variation in density for pure CO_2 at 35 °C. At this temperature (*i.e.*, close to T_c for CO_2) there is a rapid but continuous increase in density near the critical pressure (P_c). (b) Schematic representation of the change from liquid–gas equilibrium ($T < T_c$) to supercritical fluid ($T \geqslant T_c$) conditions as a substance is heated above its critical temperature at a pressure in excess of P_c.

whether the specific "supercritical" properties of the fluid offer any particular advantage. Nevertheless, even in such cases the use of scCO$_2$ can yield real benefits, such as ease of solvent separation and reductions in the use of toxic organic solvents. In this respect, *liquid* carbon dioxide is also a desirable solvent for materials applications: in fact, liquid conditions may be essential for some applications (*e.g.*, spin coating for micro-lithography, Section 3.7). When a liquid is heated above its critical temperature at pressures in excess of the critical pressure the transition from liquid to supercritical fluid is continuous [Fig. 2(b)], unlike the discontinuous transition from liquid to gas when a substance boils at pressures below P_c. Hence, under the appropriate conditions (*i.e.*, slightly below the critical temperature and pressure), liquid CO_2 may be considered as a "near-critical" fluid. This means that, while being a liquid, the substance may exhibit some SCF-like properties such as reduced viscosity and density. As a consequence, near-critical liquid CO_2 displays a limited degree of compressibility and its solvent properties may be fine-tuned with pressure, albeit to a much lesser extent than in the supercritical state. A practical advantage of working with liquid CO_2 is that relatively high solvent densities can be achieved at moderate pressures: for example, the density of liquid CO_2 at 20 °C is greater than 0.84 g cm^{-3} at pressures above 75 bar. For certain processes that operate near the critical temperature for CO_2 (31.1 °C) one may be able to choose between working with CO_2 in the liquid state or under supercritical conditions. In such cases the best choice will be determined by the specific process requirements.

1.2 Solubility of polymers in supercritical CO_2

While CO_2 is a good solvent for many non-polar (and some polar) molecules with low molecular weights,[10] it is a very poor solvent for most high molecular weight polymers under readily achievable conditions (<100 °C, <1000 bar). The only polymers shown to have good solubility in pure CO_2 under mild conditions are certain amorphous fluoropolymers and silicones.[3] This has allowed the synthesis of high molecular weight fluoropolymers [*e.g.*, poly(1H,1H-perfluorooctyl acrylate)][11] by homogeneous solution polymerisation in CO_2 (Section 2.1). The pressures and temperatures needed to dissolve a polymer in CO_2 depend on the intermolecular forces between solvent–solvent, solvent–polymer segment, and polymer segment–segment pairs in solution (*i.e.*, the interchange energy), and
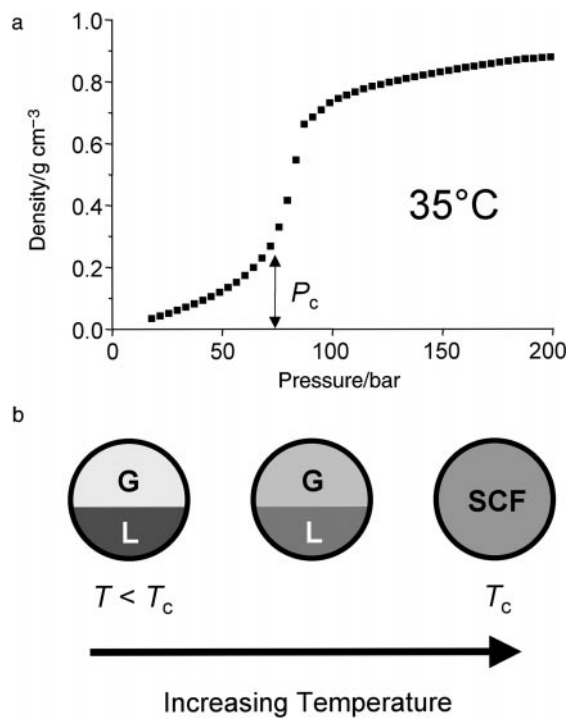
on the free volume difference between the polymer and CO_2.[12] Carbon dioxide has a low dielectric constant (relative permittivity) (1.01–1.67, depending on conditions)[13] and its polarisability (27.6×10^{-25} cm^3)[14] is close to that of gases such as methane, perfluoromethane, and fluoroform. Due to structural symmetry CO_2 does not have a dipole moment, but it does have a substantial quadrupole moment that operates over a much shorter distance scale than dipolar interactions. CO_2 is a weak solvent for non-polar polymers under most conditions since CO_2 quadrupolar interactions dominate the interchange energy as the temperature is lowered. The introduction of a degree of polarity in the polymer chain tends to lead to somewhat enhanced solubility,[15] although it is still necessary to use impractically high pressures and temperatures in order to dissolve non-fluorinated materials. It has been suggested that the anomalously high solubility of amorphous fluoropolymers may be explained by weak complexes with CO_2, or by preferential clustering of CO_2 near the fluorine atom of the C–F bonds, which are more polar than C–H bonds. Hence, fluorinated side groups may "shield" the hydrocarbon main chain from interacting with the solvent. The solubility of poly(dimethyl- and poly(phenylmethyl-silicones) is likely due to the very flexible nature of these materials that endows them with much larger free volumes in comparison with other polymers.[12] Extensive studies have been made on the solubility of both fluoropolymers and silicones in CO_2.[3,12,16] A number of researchers have used spectroscopic methods to elucidate specific CO_2–polymer interactions. FTIR studies by Kazarian *et al.*[17] have shown that CO_2 can participate in Lewis acid–base type interactions with polymers containing electron-donating groups such as carbonyls. Dardin *et al.* used *in situ* high-pressure ^{1}H and ^{19}F NMR spectroscopy to show that specific solvent–solute van der Waals interactions exist between CO_2 and certain fluorinated solutes, and that these interactions cause magnetic shielding of the fluorine nuclei.[18] Further evidence for specific solvent–solute interactions between CO_2 and fluorocarbons has come from the study of activation

parameters for the thermal decomposition of fluorinated initiators in CO_2.[19]

Whatever the precise physical basis for the unusual solubility of amorphous fluoropolymers and silicones, for practical purposes the materials chemist may consider CO_2 as a non-solvent for the majority of high molecular weight polymeric materials. While this imposes certain restrictions, the poor solvent strength of CO_2 has also been exploited in areas such as polymer fractionation (Section 3.1), selective extraction and polymer purification (Section 3.2), and the formation of polymer particles by antisolvent precipitation (Section 3.6). Supercritical CO_2 has also been shown to be an excellent non-solvating, porogenic diluent for the synthesis of well defined porous polymers (Section 2.7). Furthermore, the high solubility of amorphous fluoropolymers and siloxanes in CO_2 has allowed researchers to extend the range of CO_2-based materials applications. This has proved particularly important in the development of CO_2-soluble stabilisers for dispersion polymerisation (Section 2.3). Highly fluorinated amorphous polymers have also been employed in applications such as coatings and lithography (Section 3.7), extraction,[20,21] and the formation of aqueous microemulsions in liquid or supercritical CO_2.[22] Water-in-CO_2 microemulsions have shown considerable promise as environments for chemical reactions,[23] materials synthesis,[24] and the manipulation of hydrophilic biomolecules.[25] There are, in fact, many examples in the literature where traditional chemistry has been translated into scCO_2 *via* the use of custom-synthesized, fluorinated (or silicone-based) analogues of common surfactants, reagents, or catalysts. While this approach has proved extremely successful, it is always important to weigh the advantages gained from the use of scCO_2 against the additional cost and complexity of these new "CO_2-philic"[26] materials. In this respect, the development of methods to separate, recover and recycle surfactants and reagents may prove important.

1.3 Polymer plasticisation

Although the solubility of most polymers in CO_2 is extremely low, the solubility of CO_2 in many polymers is substantial. This can lead to a dramatic decrease in the glass transition temperature (T_g) of these materials (*i.e.*, plasticisation), even at modest pressures. For example, the T_g of polystyrene was found to be reduced by up to 50 °C under CO_2 pressures of only 25 bar.[27] It has been shown by various methods[1a] that CO_2 is a good plasticising agent for a host of polymeric materials, including polystyrene,[28–32] polyethylene,[33,34] poly-(ethylene terphthalate),[27,33,35] polyisoprene,[29] polypropy-lene,[33] poly(vinyl chloride),[27,35] nylon[33] and poly(2,6-dimethylphenylene oxide).[35] CO_2 has also been shown to plasticise polymethacrylates,[27,29–31,35–43] polycarbo-nates,[27,31,35,42,44] polyurethanes,[35,45] polyimides,[35] cross-linked elastomers[46] and networks,[47] and a number of block copolymers[29] and polymer blends.[27,48–50] Plasticisation effects are important to some degree in the majority of applications described in this review. In heterogeneous polymerisation (Sections 2.2–2.7), plasticisation may facilitate diffusion of monomer and initiator into the polymer phase. This has been demonstrated, for example, in the formation of blends by polymerisation within a CO_2-swollen host polymer (Section 2.6). Plasticisation is the underlying principle in a range of polymer processing techniques involving scCO_2, including polymer extraction (Section 3.2), impregnation (Section 3.3), and heterogeneous chemical modification (Section 3.4). It also plays an important role in the formation of microcellular polymers (Section 3.5), particulate polymers (Section 3.6) and polymer coatings (Section 3.7) *via* scCO_2 processing. While scCO_2 is not unique among solvents in its ability to plasticise polymers, it does have unusual

properties which are useful for polymer synthesis and processing. For example, many of the processing applications described in Section 3 exploit the fact that CO_2 is a good plasticiser while being a very poor solvent for the polymer. Plasticisation may also allow processing to occur at low temperatures, which is important for the treatment of thermally sensitive materials (see Section 3.6). Furthermore, since no toxic solvent residues are left in the materials, the use of CO_2 may be particularly valuable in the processing of polymers for medical applications.

1.4 CO_2 as a polymerisation medium

There are a number of factors that make carbon dioxide a desirable solvent for carrying out polymerisation reactions. From an industrial perspective, CO_2 is inexpensive, non-toxic, non-flammable, and readily available in high purity from a variety of sources.[51] In addition, the separation of solvent from product is simplified because CO_2 reverts to the gaseous state upon depressurisation, thus eliminating energy intensive drying steps. From a chemical perspective, CO_2 is relatively inert. As will be described in Section 2, this has allowed the synthesis of polymers by a wide variety of mechanisms, including free-radical chain growth, cationic chain growth, oxidative coupling, transition metal catalysis, and melt phase condensa-tion polymerisation. There are also examples of the polymer-isation of monomers in CO_2 by ionising radiation,[52] thermal ring opening,[53] and enzymatic catalysis,[54,55] both in scCO_2[54] and in supercritical fluoroform.[55] Apart from a few cases where CO_2 was deliberately copolymerised (*e.g.*, the synthesis of polycarbonates,[56] see Section 2.2), it has been found generally to be non-reactive in these processes. A selection from the range of monomers that has been polymerised or copoly-merised using CO_2 as the polymerisation medium is shown in Table 2. Carbon dioxide has been found to be inert towards free radicals and cations under common polymerisation conditions, and a large number of studies have involved these mechanisms. The absence of any detectable chain transfer to solvent in these systems is an important advantage. Carbon dioxide does react with strong nucleophiles (*e.g.*, primary amines, alkoxides), and one might therefore expect that this would preclude the possibility of polymerisation in CO_2 *via* anionic mechanisms. Nevertheless, recent studies[57] suggest that in some cases anionic (or "pseudoanionic") polymerisation may be feasible in CO_2. As discussed in Section 1.2, the only polymers shown to have significant solubility in CO_2 under practical conditions are amorphous fluoropolymers and silicones. This has allowed the synthesis of fluoropolymers by homogeneous solution polymerisation (Section 2.1). How-ever, most polymers are not soluble in carbon dioxide, thus necessitating heterogeneous polymerisation techniques for these materials (Sections 2.2–2.7).

1.5 Scope of this feature article

This article will focus on the use of CO_2 as a medium for polymer synthesis and processing. Patent literature is not covered, nor is the use of other supercritical fluids (*e.g.*, the industrial polymerisation of ethene[58]). The review covers the period up to and including mid-July 1999, with emphasis on recent developments in the last three years. Special attention is given to the use of CO_2 for the formation of polymers with well defined particle morphologies or controlled porosity, either *via* synthesis or processing.

2 Polymer synthesis using supercritical CO_2

2.1 Homogeneous polymerisation

Amorphous fluoropolymers are important in a range of technologically demanding applications, but the synthesis

Table 2 Selection of monomers which have been polymerised using carbon dioxide

1

O / CH$_2$C$_7$F$_{15}$
acrylate

ref. 11

2

CH$_2$O(CH$_2$)$_2$C$_8$F$_{17}$

ref. 68

3

CH$_2$=CF$_2$

ref. 69

4

O—R$_f$

R$_f$ = -(CH$_2$)$_2$C$_n$F$_{2n+1}$ (n = 5-7)
-(CH$_2$)$_2$N(Et)SO$_2$C$_8$F$_{17}$

ref. 71

5

CH$_2$OCH$_2$C$_3$F$_7$

ref. 71

6

CO$_2$H

ref. 73,74

7

CF$_2$=CF$_2$

ref. 76,77

8a

CF$_2$=C(F)(CF$_3$)

8b

CF$_2$=C(F)(OC$_3$F$_7$)

ref. 76

9

ref. 78,79

10

$\left(\text{O-C(O)} \right)_3$

ref. 79,155

11

ref. 79,155

12

CO$_2$H

ref. 79,155

13

H$_2$C=O

ref. 81

14

ref. 81

15

O(CH$_2$)CH(CH$_3$)$_2$

ref. 71

16

CH$_2$ONO$_2$

ref. 86

17a

ref. 57

17b

ref. 87,88,91

18

ref. 87,88,91

19

ref. 91

20

Ph—C≡C—H

ref. 92

21

ref. 93

22

ref. 98

23

ref. 99,101,102,104

24

OH

ref. 109

25

CO$_2$H

ref. 110

26

CO$_2$Me

ref. 62-65,75,112,117,118,
121,124-128,130

27a

O—C(O)Me

27b

CH$_2$=CH$_2$

ref. 119,141

28

ref. 62,63,70,78,79,85,120,
132,135

29

C(O)NH$_2$

ref. 147

30

OMe / Si / OMe / MeO / OMe

ref. 158

31

(EtO)$_3$Si—⟨⟩—Si(OEt)$_3$

ref. 158

32

HO—⟨⟩—⟨⟩—OH

+ Ph-O-C(O)-O-Ph

ref. 163,165

33

HO—R'—O—C(O)—R—C(O)—O—R'—OH

R = p-C$_6$H$_4$, m-C$_6$H$_4$
R' = C$_2$H$_4$, C$_4$H$_8$

ref. 166

34

$^+$H$_3$N—(CH$_2$)$_6$—NH$_3^+$

+

$^-$O$_2$C—(CH$_2$)$_4$—CO$_2^-$

ref. 167

35

Fe / Si

ref. 53

36

H$_3$C—⟨⟩—OH

ref. 54

and processing of these materials can be difficult due to poor solubility in most common organic solvents. The use of chlorofluorocarbon (CFC) solvents has been common for this purpose: however, strict limitations are now imposed on CFCs due to environmental issues. In a seminal paper, DeSimone *et al.* showed that amorphous fluoropolymers could be synthesized by homogeneous solution polymerisation in scCO$_2$ using thermal free-radical initiation.[11] Carbon dioxide is a very attractive alternative to CFCs since it is inexpensive, non-toxic, and non-flammable. Monomers such as 1H,1H-perfluorooctylmethyl acrylate (FOA, **1**) were polymerised in CO$_2$ using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator (50% w/v **1**, 59.4 °C, 207 bar, 48 h). The solution properties of PFOA in scCO$_2$ were investigated by small angle neutron scattering (SANS), and the second virial coefficient, A_2, for the polymer was found to be positive, confirming that CO$_2$ is a good solvent for PFOA.[59,60] The rate of AIBN decomposition in CO$_2$ was found to be approximately 2.5 times lower than the equivalent rate in benzene, presumably due to differences in the dielectric constants of the two solvents.[61] On the other hand, the efficiency of radical generation was found to be significantly higher in CO$_2$ than in benzene. This was attributed to the low viscosity of the supercritical fluid which allows facile radical diffusion into the bulk solvent. More recently, propagation rate coefficients (k_p) have been determined for styrene,[62,63] methyl methacrylate,[62–65] and butyl acrylate[63,65,66] using pulsed-laser polymerisation, and it was found that values were lower than in the bulk, indicating a solvent effect. Other fluorinated acrylates and methacrylates[67] and fluoroalkyl-derivatised styrene monomers (**2**)[68] have been polymerised or copolymerised in CO$_2$ *via* homogeneous methods. Homogeneous free-radical polymerisation has also been used to synthesize telomers of 1,1-difluoroethylene.[69] In this process, the molecular weight and molecular weight distribution appeared to be sensitive to solvent density, suggesting that manipulation of pressure could afford a means to remove telomers of a certain kinetic chain length from further reaction, thus achieving useful separations. More recently, Beuermann *et al.* described the free-radical polymerisation of styrene in scCO$_2$ under homogeneous conditions at somewhat higher pressures and temperatures (80 °C, 200–1500 bar) and in the presence of a chain transfer agent (CBr$_4$).[70] These reactions remained homogeneous due to a combination of the high pressure conditions, the relatively low molecular weight of the products (caused by chain transfer), and the fact that the polymerisation was taken to quite low monomer conversions (7.1–36.2%) (*i.e.*, the residual monomer acted as a cosolvent). In addition to homogeneous free-radical polymerisations, CO$_2$ has also been used as a medium for the homogeneous cationic polymerisation of fluorinated vinyl and cyclic ethers (**4**, **5**) using Lewis acid initiators (EtAlCl$_2$ or BF$_3$).[71] The fluorinated polymers were obtained in good yields and had molecular weights similar to those of materials synthesized using Freon-113 as the solvent.

Thus, CO$_2$ appears to be an excellent solvent medium for the synthesis and solution processing of certain fluoropolymers. There are compelling reasons for considering the use of supercritical fluid technology because the only other solvents for these fluorinated materials tend to be CFCs. However, as we have seen, most common high molecular weight polymers show negligible solubility in CO$_2$ under practicable conditions. The synthesis of these materials has therefore involved heterogeneous polymerisation techniques, as described in Sections 2.2–2.7. The lack of solubility of common polymers in CO$_2$ is sometimes described as a major disadvantage to its use as a polymerisation medium. However, it should be remembered that insolubility of the polymer in the continuous phase is actually a prerequisite for processes such as suspension, emulsion, and dispersion polymerisation, and that these heterogeneous polymerisation techniques are the methods of choice for the synthesis of many materials. As we

will see, a more serious issue is the fact that common surfactants and stabilisers tend to be ineffective in CO$_2$, which has necessitated the development of novel (and so far, more costly) alternatives (see Section 2.3). In this review, reactions have been grouped according to the observed phase behaviour, in order to underline the importance of this when considering CO$_2$ as a potential polymerisation medium. Reactions are classified using the standard terminology put forward in Arshady's methodological survey of heterogeneous polymerisation techniques.[72]

2.2 Precipitation polymerisation

A variety of polymers has been synthesized in CO$_2$ by precipitation polymerisation. The most common mechanisms have been free-radical or cationic chain growth, although a growing number of recent studies have employed transition metal catalysis. A frequently cited advantage for the use of CO$_2$ in precipitation polymerisation is that products can be isolated directly from the reactor after depressurisation as dry, solvent-free powders.

Much of the early work on the use of CO$_2$ as a polymerisation medium involved the free-radical precipitation polymerisation of industrially important vinyl monomers. This research, which is mostly described in the patent literature, will not be discussed here since it has already been reviewed in some depth.[1b] More recently, DeSimone[73] and others[74] have investigated the free-radical precipitation polymerisation of acrylic acid in scCO$_2$. The very fast propagation rate for this reaction allowed the synthesis of high molecular weight poly(acrylic acid) ($M_n \approx 150 \times 10^3$ g mol^{-1}),[73] even though the polymer precipitated from solution. It was shown that the molecular weight of the product could be controlled by the use of chain transfer agents such as ethanethiol.[73] Similarly, the use of chain transfer agents for molecular weight control has featured in studies on the polymerisation of styrene[70] and methyl methacrylate (MMA)[75] in scCO$_2$. High performance fluoropolymers have also been synthesized in CO$_2$ by free-radical precipitation polymerisation. In 1995, DeSimone and co-workers reported the copolymerisation of tetrafluoroethylene (TFE) with hexafluoropropene **8a** and with perfluoro (propyl vinyl ether) **8b**.[76] Unlike the telomers of 1,1-difluoroethylene which were synthesized by homogeneous solution polymerisation,[69] these high molecular weight copolymers precipitated as they were formed. A primary advantage of the use of CO$_2$ in this process is that the solvent contains no abstractable protons and hence the highly electrophilic species derived from the fluorolefin monomers do not chain transfer to solvent. Similar benefits were found for the free-radical homopolymerisation of TFE carried out using hybrid CO$_2$/ aqueous systems.[77] More recently, Cooper *et al.* have investigated the formation of highly cross-linked copolymers in scCO$_2$ by free-radical precipitation polymerisation.[78] High levels of divinylbenzene (DVB, **9**) cross-linker were used (55–80% w/w in the monomer mixture) and products were formed in high yields using AIBN as the initiator (65 °C, 12 h, 310 bar). A range of copolymers incorporating reactive or surface-active functional groups was also synthesized.[79] It was shown that cross-linked polymers could be synthesized in in the form of relatively uniform microspheres, even in the absence of any surfactants.[78,79] However, this particle morphology was only obtained under very specific reaction conditions and was attributed to the phase behaviour and the rigid, highly cross-linked nature of the products. Even under optimised conditions the particles showed signs of agglomeration and broad size distributions, and it was necessary to use fluorinated stabilisers in order to achieve discrete, uniform resin particles (see Section 2.3). The precipitation polymerisation of multifunctional monomers such as trimethylolpropane trimethacrylate

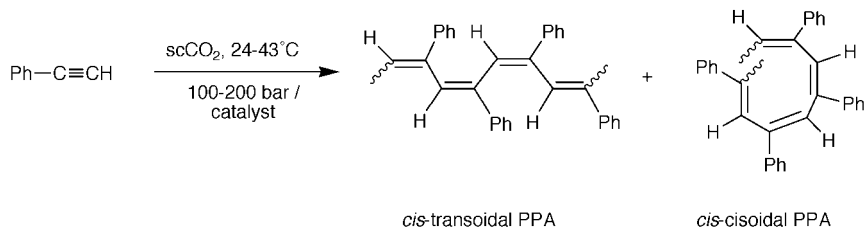(TRM, **10**)[79] and ethylene glycol dimethacrylate (EDMA, **11**)[79,80] was also investigated.

A number of studies have centred on precipitation polymerisation in liquid and supercritical CO_2 via cationic initiation.[81] Monomers such as formaldehyde and isobutene (plus other substituted alkenes) were the main focus of the early work in this area. Because of the low temperatures often used in cationic polymerisation, many of these reactions were carried out in liquid CO_2, as opposed to CO_2 in the supercritical state. Clark and DeSimone have investigated the cationic polymerisation of vinyl ethers and oxetanes (**4**, **5**, **15**) in liquid and supercritical CO_2 under both homogeneous and heterogeneous reaction conditions, depending on the nature of the monomer.[71] Since cationic polymerisation in CO_2 has been reviewed recently by Kendall et al.,[1a] only the key conclusions will be presented here. A major advantage associated with cationic polymerisation is that the high reactivity of carbocations results in fast kinetics.[82] Unfortunately, this same reactivity can lead to side reactions such as chain transfer and termination. These reactions may often be suppressed to some extent by carrying out polymerisations at low temperatures. "Living" cationic polymerisation involves the chemical stabilisation of the active propagating species, and this method can be used to produce well defined polymers and block copolymers.[83] In addition to eliminating the use of toxic organic solvents, CO_2 has certain chemical and physical advantages that make it an attractive solvent for cationic polymerisation. First, CO_2 is relatively inert toward cationic species, and polymerisations have been shown to occur without incorporation of CO_2 in the polymer backbone.[71,81] Secondly, solvent choice is important in cationic polymerisation since it affects the equilibrium between contact ion pairs and solvent-separated ion pairs at the propagating chain end. This in turn may influence the activation energy of chain transfer and termination reactions, thus determining the degree of "livingness" in a living polymerisation. Since $scCO_2$ is highly compressible, it has been suggested[71] that the solvent properties may be tuned in order to enhance the integrity of the propagating carbocationic chain ends.[84]

In addition to the preparation of polyethers, cationic initiation has been used for the dispersion polymerisation of styrene in $scCO_2$ (see Section 2.3).[85] In a quite different application, Farncomb and Nauflett prepared an energetic polymer in liquid CO_2 via the cationic precipitation polymerisation of 3-methyl-3-nitratomethyl oxetane (NIMMO, **16**).[86] The key advantages cited for the use of CO_2 in this process were reductions in hazardous waste production and improved safety due to the non-flammable nature of the solvent. Recently, Mingotaud et al. described the cationic ring-opening polymerisation of both octamethylcyclotetrasiloxane (D$_4$) and phenyloxazoline **17a**.[57] The same authors also investigated the ring-opening polymerisation of ε-caprolactone **17b** in $scCO_2$ using aluminium, yttrium, or lanthanum isopropoxide initiators. They suggest that these latter reactions proceed via an anionic or pseudoanionic mechanism, depending upon the initiator. No evidence of CO_2 incorporation was found in the polymers, despite the fact that CO_2 is known to react with some anionic species.
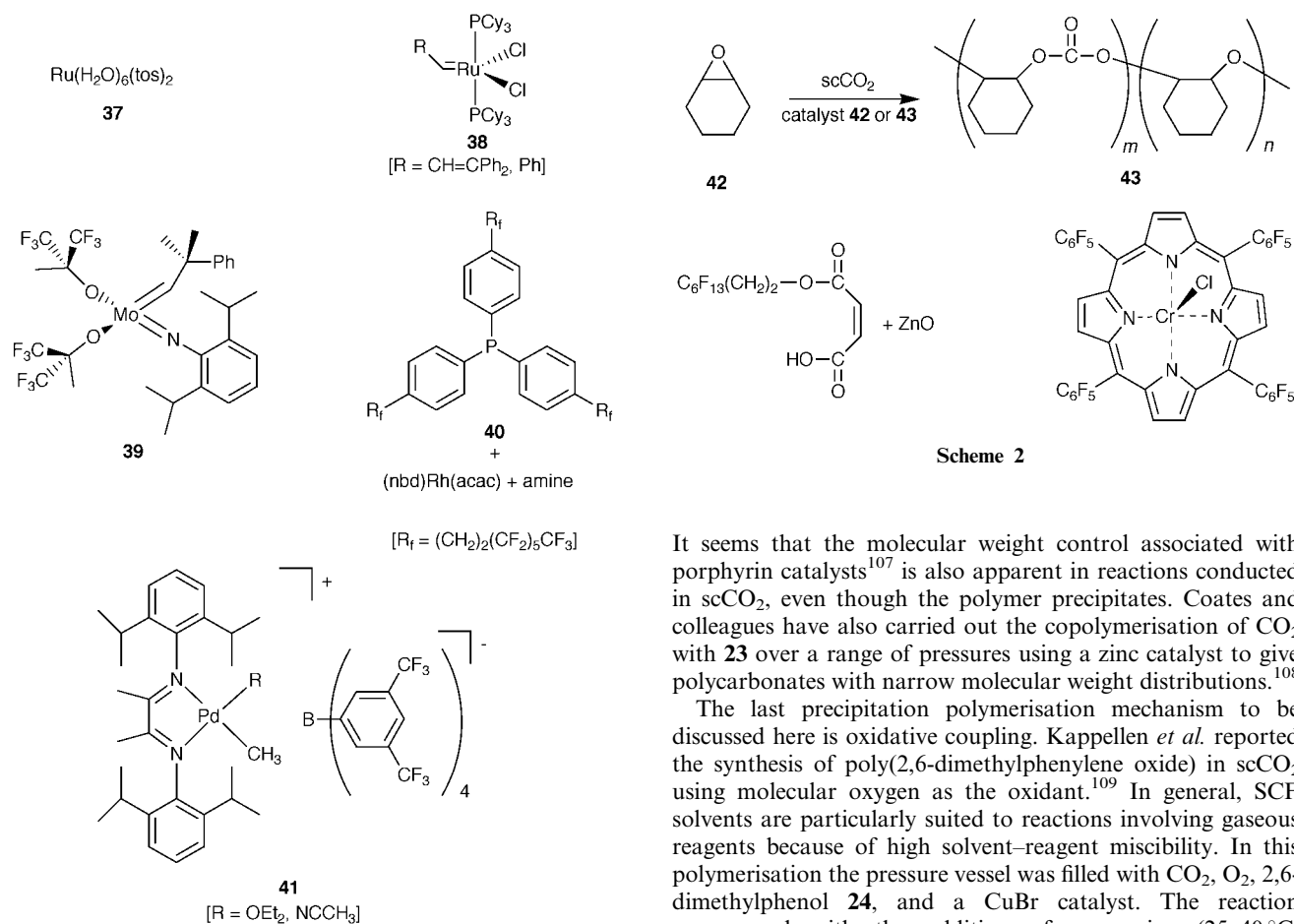
The use of transition metal catalysis for precipitation polymerisation in CO_2 has attracted much interest recently, particularly because this work has overlapped with the development of transition metal catalysts for homogeneous organic reactions in CO_2.[6] Mistele et al. described the ring-opening metathesis polymerisation (ROMP) of norbornene **18** in $scCO_2$ using a $Ru(H_2O)_6(O_3SC_6H_4Me\text{-}p)_2$ catalyst (**37**) (65 °C, 60–345 bar).[87] The catalyst was insoluble in neat CO_2 but could be solubilised in the CO_2/monomer mixture by the addition of methanol as a cosolvent. The stereochemistry of the polymer was strongly affected by the amount of methanol used in the reaction.[87,88] Fürstner et al. have shown that a ruthenium–carbene Grubbs[89] catalyst (**38**) and a molybdenum–carbene Schrock[90] catalyst (**39**) are even more active for the ROMP of norbornene in CO_2.[91] The ruthenium catalyst was also used to polymerise cis-cyclooctene **19**. Both catalysts produced high molecular weight polymers (10^5–10^6 g mol^{-1}) in good yields (up to 94%), again by precipitation polymerisation. Very recently, Leitner and colleagues have reported the synthesis of polyphenylacetylene (PPA) in liquid and supercritical CO_2 (Scheme 1) using an insoluble rhodium catalyst precursor, (nbd)Rh(acac), which was solubilised in the reaction mixture by the addition of a perfluoroalkyl-substituted triphenylphosphine ligand (**40**).[92] Polymer yields of 60–75% were reported, and the THF-soluble fraction of the PPA product had a molecular weight, M_w, of approximately 4×10^4 g mol^{-1} ($M_w/M_n = 8$–10). There was some evidence to suggest that the stereochemistry of the PPA prepared by this route was different to that of PPA synthesized in common organic solvents. Preliminary results by de Vries et al.[93] describe the polymerisation of 1-hexene in $scCO_2$ using a palladium diimine catalyst (**41**) of the type developed by Brookhart.[94] A pale yellow colour in the solution indicated that the catalyst was at least partially soluble in the CO_2/1-hexene mixture at 35 °C and pressures above 150 bar. The results were encouraging, although the turnover frequencies for the reactions in CO_2 were somewhat lower than values measured for control reactions carried out in CH_2Cl_2.[95] The phase behaviour of an ethylene–propene copolymer was also investigated,[93b] both with pure ethylene and with an 80 : 20 w/w mixture of ethylene and CO_2. Carbon dioxide was found to be a strong antisolvent for the copolymer, particularly at temperatures in the range used for the 1-hexene polymerisations. This observation raises questions about the role of CO_2 in polymerisations of this type. Monomers such as ethylene[96] and propene,[97] for example, are known to have useful solvent properties, both in the liquid and supercritical state (see Table 1 for critical parameters). One might therefore envisage transition metal catalysed polymerisations using the appropriate neat olefins (or olefin mixtures) as solvents, providing that the catalyst has sufficient solubility in the liquid/supercritical monomer.

By contrast, CO_2 has been shown to have very specific advantages as a solvent for the synthesis of aliphatic polycarbonates by precipitation polymerisation.[56] In these polymerisations the solvent is also one of the reagents, thus making use of CO_2 as an inexpensive C_1 feedstock. Darensbourg and co-workers demonstrated the copolymerisation of both propylene oxide (PO, **22**)[98] and 1,2-cyclohexene oxide (CHO, **23**)[99] with CO_2 using heterogeneous zinc catalysts. In

$Ph-C\equiv CH$ $\xrightarrow[\text{100-200 bar / catalyst}]{\text{scCO}_2,\ 24\text{-}43\,°C}$

cis-transoidal PPA   cis-cisoidal PPA

Scheme 1

Ru(H₂O)₆(tos)₂

37

38

[R = CH=CPh₂, Ph]

39

40
+
(nbd)Rh(acac) + amine

[R_f = (CH₂)₂(CF₂)₅CF₃]

41

[R = OEt₂, NCCH₃]

42

43

C₆F₁₃(CH₂)₂—O—C ... + ZnO

Scheme 2

both cases the polycarbonate products precipitated as they were formed. Catalyst efficiencies were low to average (*i.e.*, 3–370 g polymer per g Zn), possibly because of the insoluble nature of the zinc complexes.[100] In the copolymerisation of PO with CO_2[98] a small percentage (4–14%) of a cyclic side product, propylene carbonate, was always observed. The proportion of carbonate linkages in the polymer (*i.e.*, the degree of CO_2 incorporation) was in the range 70–95%, the remaining linkages being propylene ethers. Weight averaged molar masses were fairly high [$M_w = (25–150) \times 10^3$ g mol⁻¹], but molecular weight distributions were broad ($M_w/M_n = 3.4–19$). An important advance was made by Beckman and co-workers, who synthesized aliphatic polycarbonates in scCO₂ using a CO_2-soluble catalyst (Scheme 2).[101] In this study the copolymerisation of CO_2 and cyclohexene oxide was catalysed by a partially fluorinated zinc alkyl complex (**42**) with somewhat improved efficiencies (≈ 400 g polymer per g Zn). Phase behaviour studies were undertaken on the CO₂/CHO system in order to determine the best conditions for copolymerisation.[102,103] Despite the fact that the catalyst was soluble, molecular weight distributions were still very broad ($M_w/M_n = 2.4–27$),[101] indicating little control over the polymerisation. Recently, Mang *et al.* have synthesized a partially fluorinated chromium porphyrin complex[104] (**43**) which was found to be soluble in both neat scCO₂ and in scCO₂/CHO mixtures.[105] In the presence of a base (dimethylaminopyridine), complex **43** was shown to catalyse the copolymerisation of CHO and CO_2. Polycarbonate was formed in good yields and the products exhibited high degrees of CO_2 incorporation (90–97%) as determined by ¹H NMR. Catalyst efficiencies were substantially higher than in previous systems (up to 3900 g polymer per g Cr), but the most striking difference was the narrow molecular weight distribution ($M_w/M_n < 1.4$) which was observed for all of the polymers prepared *via* this route.[106]

It seems that the molecular weight control associated with porphyrin catalysts[107] is also apparent in reactions conducted in scCO₂, even though the polymer precipitates. Coates and colleagues have also carried out the copolymerisation of CO_2 with **23** over a range of pressures using a zinc catalyst to give polycarbonates with narrow molecular weight distributions.[108]

The last precipitation polymerisation mechanism to be discussed here is oxidative coupling. Kappellen *et al.* reported the synthesis of poly(2,6-dimethylphenylene oxide) in scCO₂ using molecular oxygen as the oxidant.[109] In general, SCF solvents are particularly suited to reactions involving gaseous reagents because of high solvent–reagent miscibility. In this polymerisation the pressure vessel was filled with CO₂, O₂, 2,6-dimethylphenol **24**, and a CuBr catalyst. The reaction commenced with the addition of an amine (25–40 °C, 345 bar) to yield poly(2,6-dimethylphenylene oxide) in good yield (up to 86%) and with high molecular weight (up to 1.7×10^4 g mol⁻¹). In some reactions CO_2-soluble polymeric amines were used [poly(FOA-co-vinylpyridine) or poly(FOA-co-2-N,N-dimethylaminoethyl acrylate)]. The addition of a CO_2-soluble block copolymer surfactant led to improved yields and molecular weights *via* a dispersion polymerisation route (see Section 2.3). Armes and co-workers have synthesized polypyrrole in both scCO₂ and supercritical fluoroform, using *in situ* pyrrole generation *via* the thermal decarboxylation of 2-carboxypyrrole **25** (80–110 °C, 50–150 bar).[110] Two chemical oxidants were investigated: FeCl₃ and Fe(OTf)₃ (OTf = CF₃SO₃⁻). The use of Fe(OTf)₃ gave better yields (up to 87%), probably because of the enhanced catalyst and monomer solubility observed under those conditions. The pressed pellet conductivity (four point probe technique) for polypyrrole prepared in scCO₂ was found to be in the range $(0.3–5) \times 10^{-2}$ S cm⁻¹. These values are rather low in comparison with samples prepared by more conventional methods, although this was probably a result of overoxidation caused by the elevated temperatures, rather than any deleterious influence arising from the choice of solvent. Polymers prepared in scCO₂ exhibited unusual fibrillar morphologies that were quite distinct from the globular morphology typical of polypyrrole synthesized in water. Whilst being a promising organic conductor, polypyrrole is difficult to process because it is insoluble, hard, and brittle. These problems can be addressed by blending polypyrrole with a polymer which has better mechanical properties, either by direct blending or by *in situ* polymerisation. Fu *et al.* showed that polyurethane foams could be impregnated with an oxidant [Fe(OTf)₃] using scCO₂ as the solvent.[111] When the doped material was exposed to pyrrole vapour an *in situ* polymerisation occurred within the polyurethane matrix to form composite materials with conductivities as high as 3×10^{-2} S cm⁻¹. Post-polymerisation clean up of the foams was attempted *via* supercritical fluid

extraction (SFE) to remove the reaction by-products, but this showed only limited success due to the low solubility of the by-products in CO_2. The use of scCO$_2$ for extraction is discussed in more detail in Section 3.2.

2.3 Dispersion polymerisation

While CO_2 is a good solvent for the precipitation polymerisation of many CO_2-soluble monomers, by no means all polymers can be prepared readily by this route. As a result, several groups have worked on the development of free-radical dispersion polymerisation techniques using CO_2 as the continuous phase. Given the relatively small number of polymerisations conducted using CO_2 thus far, it is not easy to predict *a priori* which systems will give rise to high molecular weight products and high monomer conversions by precipitation polymerisation, and which systems will require the use of dispersion polymerisation techniques. In addition to the obvious experimental variables (*i.e.*, concentration, temperature, pressure), factors such as polymerisation rate, polymer plasticisation, and the solubility (or swelling) of the polymer in its monomer will affect primary particle nucleation, and hence be important in determining the best polymerisation conditions. For example, the free-radical precipitation polymerisation of acrylic acid in CO_2 gave high molecular weight products and monomer conversions of >90%,[73] whereas the unstabilised free-radical precipitation polymerisation of MMA under very similar conditions resulted in relatively low molecular weight products and conversions of <40%.[112]

In contrast to emulsion polymerisation[113] where the monomer has very low solubility in the continuous phase, dispersion polymerisation is characterised by initially homogeneous conditions.[72,114] The resulting polymer is insoluble in the dispersion medium and therefore phase separation occurs at an early stage in the reaction. The precise point at which this happens will of course depend on the solvency of the continuous phase for the early products of the polymerisation. Common solvents for the free-radical dispersion polymerisation of lipophilic monomers such as styrene and MMA are hydrocarbons or C_1–C_5 alcohols. Particle dispersions produced in the absence of any stabiliser are not sufficiently stable and tend to coagulate during their formation. The addition of a small amount of an appropriate stabiliser (or "surfactant") to the polymerisation mixture produces a stable dispersion, which is typically referred to as a polymer dispersion, a colloidal dispersion, or a latex. The stabilisation mechanism in dispersion polymerisation is usually steric in nature, whereby a layer of stabiliser adsorbed (or grafted) at the polymer–solvent interface imparts long-range steric repulsions between particles. These forces compensate for short-range van der Waals attractions, thus preventing flocculation of the dispersion. This mechanism differs from electrostatic stabilisation which is encountered in emulsion polymerisation.[113–115] Common steric stabilisers for hydrocarbon dispersions include methacrylic polymers carrying oligostearic grafts (*i.e.*, comb-type stabilisers) and polymerisable oligomeric species (*i.e.*, macromonomers). A wide range of polar organic polymers [*e.g.*, poly(vinylpyrrolidone), poly(vinyl alcohol)] have been used as stabilisers for dispersions in alcohols and other polar solvents. Under the correct conditions, dispersion polymerisation gives rise to well defined spherical particles, typically in the size range 100 nm–10 µm. Dispersion polymerisation is an important process, and the use of CO_2 as a solvent has the potential to eliminate large volumes of organic solvents. However, common stabilisers have been found to be either insoluble in CO_2[116] or, if soluble, ineffective for dispersion polymerisation in this solvent.

In 1994, DeSimone reported the first example of free-radical dispersion polymerisation in scCO$_2$.[112] In the absence of any stabilisers, the precipitation polymerisation of MMA **26** in scCO$_2$ led to poly(methyl methacrylate) (PMMA) with relatively low molecular weights ($(77–149) \times 10^3$ g mol^{-1}) and low monomer conversions (10–40%). In the presence of 2–4% w/v of a CO_2-soluble polymer [PFOA,[11] **44**, $M_n = 1.1 \times 10^4$ or 2.0×10^5 g mol^{-1}], the phase behaviour was quite different. As the reaction proceeded (65 °C, 204 bar, AIBN), a stable, opaque-white colloidal dispersion was formed in the reaction vessel. Product molecular weights ($(190–325) \times 10^3$ g mol^{-1}) and monomer conversions (>90%) were much improved under these conditions, and the polymer, PMMA, could be recovered from the reaction vessel as a dry, free-flowing powder immediately upon venting the CO_2. When examined by scanning electron microscopy, the product was found to consist of uniform spherical particles, with average diameters in the range 1.2–2.5 µm. All of these observations were consistent with a dispersion polymerisation mechanism, and it was postulated that PFOA was an effective amphiphatic stabiliser because it contained a lipophilic backbone that could anchor onto the acrylic surface of the growing polymer particles. The CO_2-philic nature of the fluoroalkyl substituents on the stabiliser caused extension of the PFOA chain trajectory into the continuous phase, thus giving rise to steric stabilisation and preventing particle flocculation (Fig. 3). These initial findings have prompted a large number of subsequent investigations by the DeSimone group and others, particularly focusing on the free-radical dispersion polymerisation of MMA and styrene in scCO$_2$. DeSimone has made more detailed studies on the use of PFOA as a stabiliser for the dispersion polymerisation of MMA[117,118] and, more recently, vinyl acetate (Vac, **27a**)[119] and styrene (**28**).[120] The particle morphology of polystyrene[120] synthesized by dispersion polymerisation in scCO$_2$ is shown in Fig. 4. Hsiao *et al.* optimised the dispersion polymerisation of MMA in CO_2 using PFOA, and found that very uniform PMMA particles could be formed with low particle size distributions (PSD = 1.01–1.21).[117] The phase behaviour of PFOA in CO_2 (1–5 wt% PFOA) was also investigated in some detail. PFOA and its methacrylate analogue [PFOMA, **45**] have been shown to be good stabilisers for the dispersion polymerisation of styrene in CO_2 by similar methods (Fig. 4).[120] Random copolymers of FOA and styrene were synthesized as stabilisers for the dispersion polymerisation of 2,6-dimethylphenol in scCO$_2$ by oxidative coupling polymerisation,[109] although these polymers were not as effective as diblock copolymer stabilisers (see below). PFOA has also been used as a stabiliser for the preparation of poly(MMA-co-butyl acrylate) dispersions for coating applications.[121] A rather surprising discovery was made by Hsiao and DeSimone, who showed that the presence of helium in CO_2 could have significant effects on the average particle sizes and particle size distributions of PMMA samples synthesized in scCO$_2$ using PFOA as the stabiliser.[118] Solvatochromatic studies suggested that this was due to a decrease in the solvent strength of the continuous phase.[122] In addition to its use in dispersion polymerisation, PFOA has been employed for the
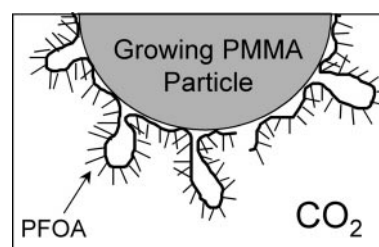

Fig. 3 Steric stabilisation in the dispersion polymerisation of MMA in CO_2 using stabiliser **44** (redrawn from ref. 112).
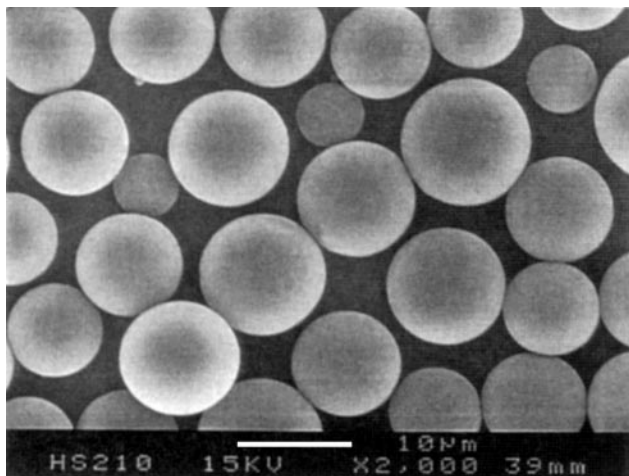
Fig. 4 SEM of polystyrene particles synthesized in scCO$_2$ by dispersion polymerisation using 1.0% w/w stabiliser **44** (reproduced with permission from ref. 120, copyright Wiley Interscience). Reaction conditions: AIBN (1% w/w), 370($\pm$20) bar, 35 °C, 40 h. Conversion = 92.3%, $M_n = 3.02 \times 10^4$ g mol^{-1}, $M_w/M_n = 3.8$, average particle diameter = 9.6 µm (PSD = 1.10).
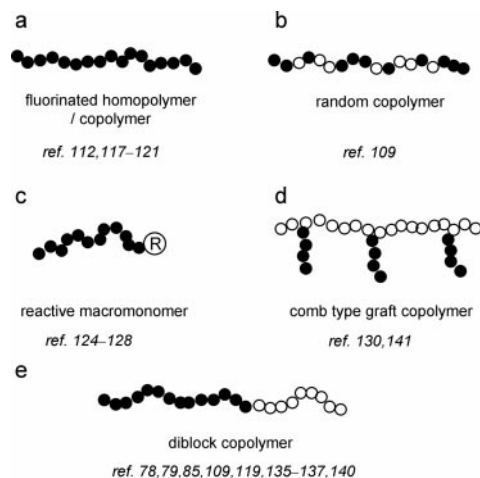

Fig. 5 Stabiliser morphologies used for dispersion polymerisation in CO$_2$. Filled circles = CO$_2$-philic monomer units, open circles = CO$_2$-phobic monomer units, R = reactive polymerisable end-group.

production of polymer microparticles by antisolvent precipitation in CO$_2$ (see Section 3.6). There have also been a number of elegant accompanying studies on the solution properties of PFOA (and variants thereof) in CO$_2$, particularly concerning micellisation phenomena and the effect of varying CO$_2$ density.[59,123]

44

45   **46**
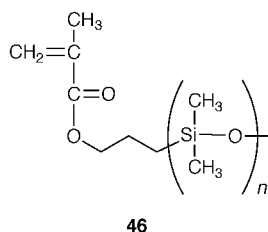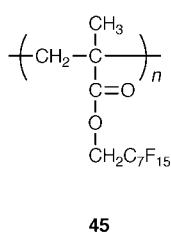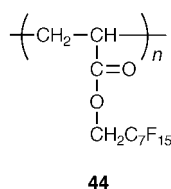
Building on the success of fluorinated (meth)acrylate homopolymers such as PFOA and PFOMA, a range of other stabilisers has been synthesized and evaluated for dispersion polymerisation in scCO$_2$. The main types of stabiliser morphologies investigated are shown in Fig. 5.

Silicone polymers are attractive as stabilisers, primarily because they are soluble in CO$_2$ and considerably less expensive than their fluorinated counterparts. Silicones are also soluble in a range of conventional organic solvents, which makes the characterisation of these materials somewhat easier than in the case of high molecular weight fluoropolymers. In 1996, Shaffer *et al.* reported the dispersion polymerisation of MMA in CO$_2$ using a commercially available methacrylate-terminated poly-(dimethylsiloxane) (PDMS) macromonomer (**46**).[124] These polymerisations were either carried out in scCO$_2$ using AIBN initiation (65 °C, 340 bar, 4 h), or in liquid CO$_2$ (30 °C, 69 bar, 21 h) using a low-temperature radical initiator [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)]. High molecular weight PMMA [$M_n = (123–390) \times 10^3$ g mol^{-1}] was formed in

good yields. The best yields and molecular weights (and the most regular spherical particle morphologies) were obtained in scCO$_2$ using rather high stabiliser concentrations (3.5–16% w/w based on monomer). It was shown that only a fraction of the macromonomer was actually copolymerised with the PMMA, and the role of the non-grafted PDMS was not clear. O'Neill *et al.* have also investigated the dispersion polymerisation of MMA in scCO$_2$ using PDMS macro-monomer stabilisers.[125,126] *In situ* turbidimetry was used to study the particle formation and growth regimes in detail, and it was concluded that the mechanism of stabilisation was complicated because of changes in the composition and solvent quality of the continuous phase over the course of the reaction. In particular, because neat CO$_2$ is a mediocre solvent for PDMS, the dispersions showed a tendency to flocculate before polymerisation was complete due to loss of solvation as the monomer was depleted. Very recently, Howdle and co-workers used the same type of PDMS macromonomer stabiliser for the dispersion polymerisation of MMA in scCO$_2$.[127,128] It was demonstrated[128] that both polymer yields and molecular weights were strongly influenced by mixing phenomena, particularly when higher AIBN concentrations were used (1% w/w AIBN compared to 0.33% w/w used by Shaffer *et al.*[124]). Somewhat surprisingly, improved yields and molecular weights were obtained in the *absence* of any stirring in the autoclave. After a series of control experiments, the authors concluded that some form of radical–metal termination reaction was occurring between propagating radicals and the steel walls of the reaction vessel. In the absence of stirring, a high molecular weight PMMA film was deposited on the walls of the reactor, thus preventing this termination reaction. It was suggested that the deposition of this film was hindered by efficient agitation, and that this was the reason for the low monomer conversions and low molecular weights under stirred conditions.[128,129] If the hypothesis is correct, this "wall effect" could have important implications for CO$_2$-based radical polymerisations, which are typically conducted in unlined autoclaves constructed of stainless steel or other high-strength alloys.

Lepillieur and Beckman synthesized a series of surfactants based on a poly(MMA-co-hydroxyethyl methacrylate) backbone with varying percentages of a CO$_2$-philic poly(perfluoropropylene oxide) graft (**47**).[130] In a sense, this structure is the reverse of the polymer studied by DeSimone (**48**) which consisted of a highly CO$_2$-philic PFOA backbone with relatively CO$_2$-phobic poly(ethylene oxide) grafts.[123d,131] Beckman's stabilisers were effective for the free-

radical dispersion polymerisation of MMA in scCO$_2$, and studies were made to find the optimum "anchor-to-soluble balance" (*i.e.*, the most effective ratio between the CO$_2$-phobic backbone and the CO$_2$-philic solubilising grafts). Interestingly, the authors also gave a theoretical analysis of the pressure changes observed during polymerisation and this was used to estimate the mean polymerisation rate, although Canelas and DeSimone have questioned the validity of using pressure monitoring to calculate reaction rates, at least for the polymerisation of styrene by dispersion polymerisation.[132]

Block copolymers have been used extensively as stabilisers for dispersion polymerisation in CO$_2$. To complement these studies, interfacial tension measurements have been made for CO$_2$-soluble diblock copolymer stabilisers at the polymer–CO$_2$ interface.[133] Investigations of this type are very useful for rationalising structure–property relationships for CO$_2$-based surfactants.[134] DeSimone has developed techniques for the synthesis of a range of amphiphilic diblock copolymer stabilisers for the dispersion polymerisation of styrene[85,132,135] and vinyl acetate.[119] Diblock copolymer stabilisers have also been used for the synthesis of PMMA[136,137] and cross-linked copolymers[78,79] by similar techniques. Most of the diblock copolymers used for dispersion polymerisation in scCO$_2$ have contained a CO$_2$-philic block and a lipophilic anchoring block. The CO$_2$-philic block has typically consisted of a fluorinated polyacrylate (PFOA),[109,119,135] fluorinated polymethacrylate (PFMA),[78,79,136,137] or PDMS.[119,132] The most common lipophilic anchoring components have been polystyrene (PS)[132,135] or PMMA,[78,79,136,137] chosen for maximum compatibility with the dispersed polymer phase. An important general parameter for stabilisers in dispersion polymerisation is the anchor-to-soluble balance. In the case of diblock copolymers for use in CO$_2$, this corresponds to the relative block lengths of the CO$_2$-philic segment and the CO$_2$-phobic anchoring segment.

Canelas *et al.* showed that PS-*b*-PFOA stabilisers (**49**) are very effective for the free-radical dispersion polymerisation of styrene in scCO$_2$ (AIBN, 65 °C, 345 bar, 24 h), and that the total molecular weight of the stabiliser has a strong effect on the average particle size and particle size distribution of the resulting colloidal polystyrene.[135] This stabiliser was also found to be effective in the dispersion polymerisation of 2,6-dimethylphenol in CO$_2$ by oxidative coupling.[109] Taking advantage of the somewhat lower cost of silicone-based materials, Canelas and DeSimone carried out a detailed study on the use of PS-*b*-PDMS stabilisers (**50**), again for the dispersion polymerisation of styrene.[132] Stabiliser concentrations of 2.5–15% based on monomer were used, and the average particle size varied from 1.15 down to 0.31 μm,

depending on the stabiliser concentration. The PS particle sizes, molecular weights, and molecular weight distributions were also found to be influenced quite significantly by the density of the CO$_2$ continuous phase (*i.e.*, the pressure), and also the presence of helium (as observed for the dispersion polymerisation of MMA in CO$_2$[118]). Control experiments using heptane as the solvent were not as successful as those conducted in CO$_2$, and the authors suggested that this may be due to plasticisation of the polymer by CO$_2$ which facilitates monomer diffusion to the growing chain ends.[132] If this is the case, it may point to a specific advantage of using CO$_2$ in polymerisations of this type.

Broadly similar results were obtained for both the dispersion polymerisation of MMA[137] and divinylbenzene[79] in scCO$_2$ using PMMA-*b*-PFMA stabilisers (**51**). In particular, it was shown that diblock copolymers could be used to produce highly cross-linked resins in the form of well defined spherical particles (mean diameter ≈400 nm, Fig. 6).[79] The PMMA-*b*-PFMA stabilisers were synthesized by a modified screened anionic polymerisation (SAP) method,[136] which allows accu-

Fig. 6 SEM of cross-linked DVB particles synthesized in scCO$_2$ using 3.0% w/w stabiliser **51**. Reaction conditions: AIBN (8% w/w), 310(±15) bar, 65 °C, 24 h. Conversion = 96%, average particle diameter = 410 nm (PSD = 1.16) (see refs. 78 and 79).

rate control of the relative block lengths. It was found that both the overall molecular weight of the stabiliser and the anchor-to-soluble balance had a pronounced effect on polymer yields and particle morphologies.[137,138]

Very recently, Yates et al. have described the synthesis of a CO_2-soluble surfactant [PDMS-b-PMA] consisting of a CO_2-philic PDMS block and a hydrophilic polymethacrylic acid (PMA) block (52).[139] Uniform PMMA particles could be synthesized in scCO_2 by dispersion polymerisation using either this stabiliser or a commercially available graft copolymer surfactant (PDMS-g-pyrrolidonecarboxylic acid, 53).[140] When mixtures of both stabilisers were used, smaller, more regular PMMA particles were formed. The PDMS-b-PMA stabiliser is particularly interesting because, in contrast to stabilisers 44–51, it allows the formation of water-dispersible PMMA powders. This is due to the "ambidextrous" nature of the surfactant, which can provide stabilisation in both water and in CO_2 (Fig. 7).

The synthesis of poly(vinyl acetate) (PVAc) and copolymers of vinyl acetate and ethylene was carried out by free-radical dispersion polymerisation both in liquid CO_2 (diisobutyryl peroxide, 27 °C, 155 bar, 18 h) and scCO_2 (AIBN, 65 °C, 352 bar, 18 h).[119] In situ turbidimetry was used to monitor dispersed-phase volumes, particle sizes, and number densities during the polymerisation, and also to give the final particle sizes at the end of the polymerisations. A range of stabilisers was evaluated, including PFOA homopolymer, PDMS homopolymer, a vinyl-terminated PDMS macromonomer, and two specifically tailored block copolymers, PVAc-b-PFOA 54, and PVAc-b-PDMS 55. Some of the best results were obtained using stabiliser 54, which gave rise to stable PVAc dispersions and almost quantitative monomer conversions. The PDMS-based stabilisers were incapable of stabilising the dispersions in the absence of a cosolvent such as n-heptane, although Rindfleisch et al. have recently reported the dispersion polymerisation of vinyl acetate in scCO_2 using comb-like PDMS-based graft copolymers.[141]

54

55

56
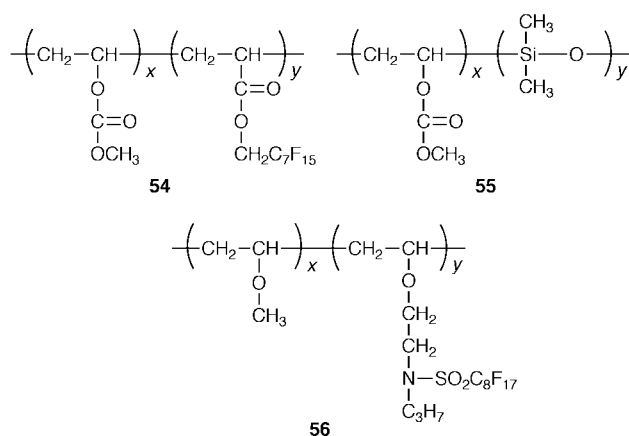
In addition to the use of diblock copolymer stabilisers in free-radical dispersion polymerisations, Clark et al. have employed a similar copolymer 56 for the cationic dispersion
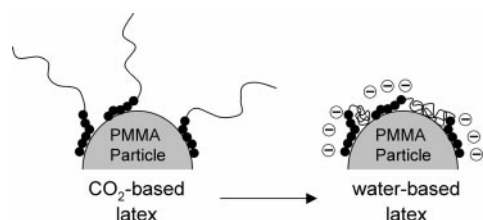
Fig. 7 Illustration of the "ambidextrous" nature of surfactant 52 (redrawn from ref. 140). In CO_2 the PDMS chains extend into the continuous phase, thus imparting steric stabilisation. In buffered water some of the methacrylic acid groups in the surfactant ionise to produce an electrostatically stabilised latex.

polymerisation of styrene in CO_2.[85] This stabiliser was synthesized from vinyl ether monomers, as opposed to the acrylate, methacrylate, or siloxane monomers used in stabilisers 49–55.[142] The cationic dispersion polymerisation of styrene was carried out in liquid CO_2 using $TiCl_4$ as the initiator (15–25 °C, 330 bar, 4 h) in the presence of 1–4% w/w stabiliser 56, to yield polystyrene in high yields (up to 95%) with number-averaged molecular weights in the range (0.4–3.1) × 10^4 g mol^{-1}. In the absence of stabiliser 56, yields and molecular weights were significantly lower (<60%, <6.3 × 10^3 g mol^{-1}). According to the authors, this is the first example of cationic dispersion polymerisation in any solvent medium.

To complement the experimental studies described above, Johnston and co-workers have developed lattice-fluid self-consistent field theory (LFSCF) to describe the stabilisation of polymer dispersions in compressible fluids.[143] Further insights into the mechanism of steric stabilisation in scCO_2 have arisen from the study of poly(2-ethylhexyl acrylate) (PEHA) emulsions by turbidimetry, tensiometry, and dynamic light scattering measurements.[144,145] In particular, the critical flocculation density was determined for emulsions of PEHA in CO_2 stabilised by surfactants such as PFOA, PS-b-PFOA, and a triblock copolymer, PFOA-b-PVAc-b-PFOA.

2.4 Emulsion and suspension polymerisation

In emulsion[113] and suspension[146] polymerisation the monomer has very low solubility in the continuous phase. Most common monomers studied so far have been found to be quite soluble in CO_2 at moderate temperatures and pressures, and therefore few examples exist of CO_2-based emulsion or suspension polymerisations. Beckman has investigated the water-in-oil or "inverse" emulsion polymerisation of acrylamide in scCO_2 (AIBN, 65 °C, 352 bar, 1 h).[147,148] An amide functionalised perfluoropolyether surfactant (57) was used to promote latex stabilisation. The latex was observed to be more stable in the presence of surfactant 57, although high monomer conversions and molecular weights were also obtained without the stabiliser. Since water and CO_2 have very low miscibility, the development of other inverse emulsion and suspension polymerisation techniques is likely to be a profitable area of research, particularly given the recent advances in the synthesis of surfactants for the formation of water-in-CO_2 microemulsions.[22–25] In principle, the use of CO_2 as a medium for the oil-in-oil emulsion or suspension polymerisation of lipophilic monomers might also be a possibility, providing that the monomers exhibit sufficient miscibility gaps at reasonable CO_2 densities. For example, Beckman has carried out the copolymerisation of cyclohexene oxide in scCO_2 under conditions where a CO_2-rich layer and a monomer-rich layer were observed from the outset, although no attempt was made to emulsify the two phases.[103] Other studies have shown that perfluorocarbon liquids are quite versatile solvents for the suspension polymerisation of a range of lipophilic and hydrophilic monomers, but the high cost of these solvents is a major drawback.[149] Carbon dioxide could be an attractive alternative for certain processes of this type.

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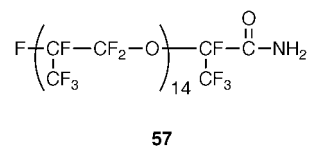
A quite different approach was taken by Quadir et al., who investigated the emulsion polymerisation of MMA in hybrid CO_2/water mixtures.[150] In these studies the emulsion was formed in the aqueous phase and not in the CO_2 layer.

2.5 Porous polymers

The synthesis of well defined porous polymers is an extremely important area of research.[151] Carbon dioxide has been used as a foaming agent for the formation of microcellular polymer foams (see Section 3.5), but until recently there were few examples of the preparation of porous polymers *via* polymerisation using scCO$_2$ as a solvent. Carbon dioxide is a particularly attractive alternative medium for the preparation of porous polymers since conventional processes often require large volumes of "porogenic" organic solvents, traces of which will tend to be trapped within the polymeric matrix. This section describes the use of scCO$_2$ for the preparation of polymeric materials with pore sizes spanning a very broad range (*i.e.*, from microcellular foams down to macroporous resins and mesoporous/microporous aerogels). These methods can obviate the need for any toxic solvents and lead to materials that contain no solvent residues.
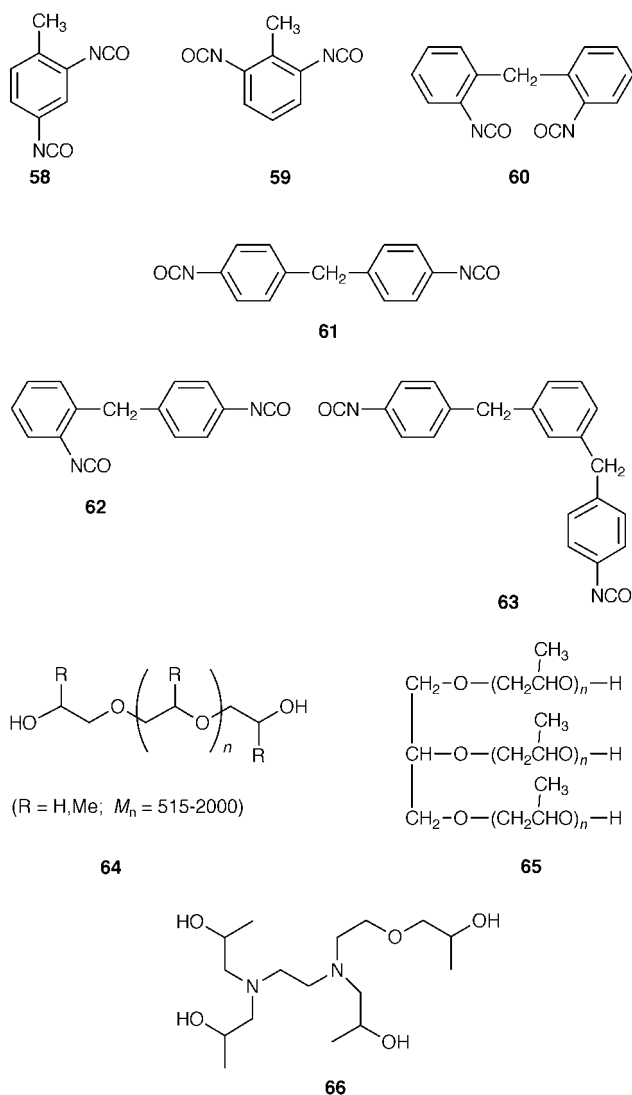
Parks and Beckman reported the generation of microcellular polyurethane foams *via* polymerisation in carbon dioxide.[152] In these studies, a range of diisocyanates (**58–63**) was treated with various propylene oxide and ethylene oxide polyols (**64–66**) in CO$_2$ (25–40 °C, 50–300 bar, 24 h) to form cross-linked polyurethanes. The reaction conditions and monomer compositions determined whether or not phase separation occurred during the course of the polymerisation. Phase separation led to the generation of a polymer-rich phase and a CO$_2$-rich phase, the latter of which became pores upon removal of the CO$_2$. This process produced microcellular foams with mean cell diameters in the range 30–180 μm, depending on the reaction conditions. Cell densities as high as 1.2×10^7 per cm^3 could be obtained, leading to materials with low bulk densities (0.2–0.4 g cm^{-3}). The internal structure of a typical foam synthesized by this route is shown in Fig. 8(a). The authors rationalised the pore growth during the venting procedure (or "pressure quench") in the following manner. As the CO$_2$ was vented at the end of the reaction, pores continued to nucleate in the polymer-rich regions, and pore growth occurred *via* two mechanisms: by diffusion of the CO$_2$ from the polymer-rich regions into the pores and by CO$_2$ expansion (*i.e.*, boiling of liquid CO$_2$ at reduced pressure). Pore growth *via* gas expansion could only occur while the polymer remained plasticised[45] and in the rubbery state. When sufficient CO$_2$ had diffused from the polymer rich regions such that the T_g for the material was near to or above the foaming temperature, then pore growth due to gas expansion was curtailed. Higher CO$_2$ pressures (and hence higher fluid densities) provided more CO$_2$ molecules for foaming, generated a lower interfacial tension and viscosity in the polymer matrix, and thus produced a higher cell density. The variation in cell size for foams synthesized from different diisocyanates could be explained by the variation in T_g of the resulting polymers. In general, the materials with the higher T_g values allowed the least opportunity for CO$_2$ expansion and therefore gave rise to the lowest average cell sizes. Increasing the degree of cross-linking in the materials gave rise to smaller cells for the same reason. In a related study, Enick *et al.* investigated the synthesis of fluoroether polyurethanes in CO$_2$ by similar methods.[153] Two fluorinated diols (Fluorolink D + T) and a fluorinated diisocyanate were used. Dibutyltin dilaurate exhibited sufficient solubility in the CO$_2$–monomer mixture to be used as a catalyst. Due to the highly fluorinated nature of these materials, the resultant polyurethane was completely soluble in a single, CO$_2$-rich phase at total initial precursor concentrations of up to 4 wt%. A CO$_2$-rich fluid phase and a polymer-rich liquid phase coexisted at precursor concentrations of 5–38 wt%. At precursor concentrations of 39–50 wt%, a single polymer-rich liquid phase was observed. Removal of the CO$_2$ *via* depressurisation yielded an elastomeric polyurethane product, although no details were given concerning the resulting polymer morphology.

There has been much interest recently in the synthesis and applications of cross-linked macroporous monoliths (*e.g.*, continuous porous separation media as potential replacements for packed porous beads).[154] Typically, a mould is filled with a polymerisation mixture containing a cross-linking monomer, functional comonomers, initiator, and a porogenic solvent (or "diluent"). This mixture is then polymerised, either thermally or photochemically, to form a continuous porous monolith which conforms to the shape of the mould. By carefully choosing monomer concentration, initiator concentration, and the nature and composition of the porogenic diluent, it is possible to produce polymers with well defined pore structures by this route. However, one disadvantage of the process is that rather large volumes of porogenic organic solvents are required in the synthesis (ratio of solvent to monomer $\approx 1 : 1$). Furthermore, it may be difficult to remove all of this solvent from the polymer matrix at the end of the reaction. Cooper and Holmes have shown that scCO$_2$ is an excellent porogenic diluent for the formation of cross-linked macroporous monoliths.[155] The studies focused on the free-radical polymerisation of cross-linking monomers such as TRM **10** and EDMA **11**, and the copolymerisation of polar functional monomers such as methacrylic acid **12**. In a typical experiment (see Fig. 9), a high-pressure reactor (equipped with a sapphire window) was loaded with monomer and initiator (AIBN, 2% w/v based on monomer). The vessel was then filled with liquid CO$_2$ such that the concentration of monomer in the CO$_2$ solution was in the range 40–60% v/v. The reactor was heated
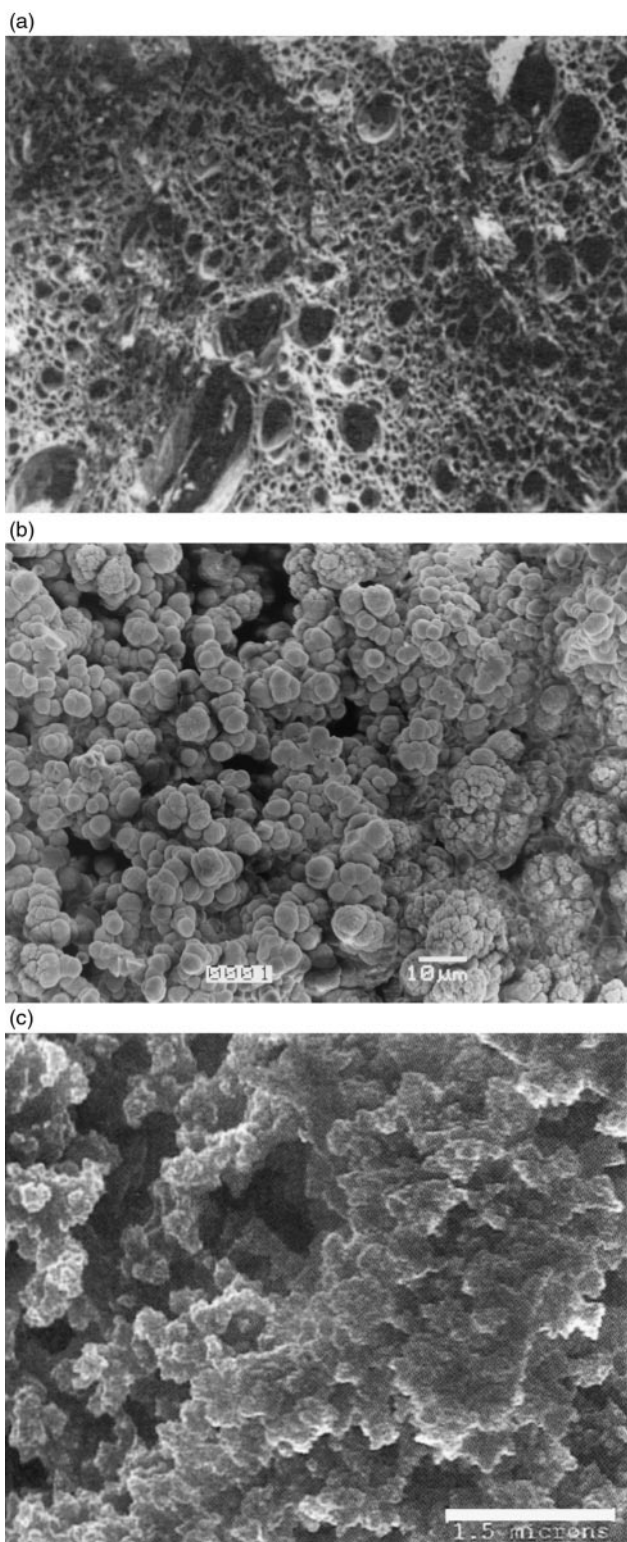
(a)

(b)

(c)

Fig. 8 SEMs of various porous polymers synthesized in scCO₂. (a) Microcellular polyurethane foam synthesized in scCO₂ (average cell size = 56.2 ± 29.0 μm, cell density = 1.1 × 10⁷ per cm³, reproduced with permission from ref. 152(*b*), copyright Society of Plastics Engineers. (b) Macroporous polymer synthesized from monomer **10** in scCO₂. Median pore diameter = 7.9 μm, surface area = 5.2 m² g⁻¹ (scale bar = 10 μm) (see ref. 155). (c) Mesoporous silica aerogel synthesized by sol–gel polymerisation of **30** in scCO₂ (scale bar = 1.5 μm), reproduced with permission from ref. 158, copyright American Chemical Society. Due to the large variation in average pore size in these samples the scale differs in images (a)–(c).

(50 °C, 12 h) to initiate polymerisation. At the beginning of the reaction a homogeneous solution was observed. As the reaction proceeded the solution became first translucent (due to gelation of the polymer) and then white and opaque (due to polymer
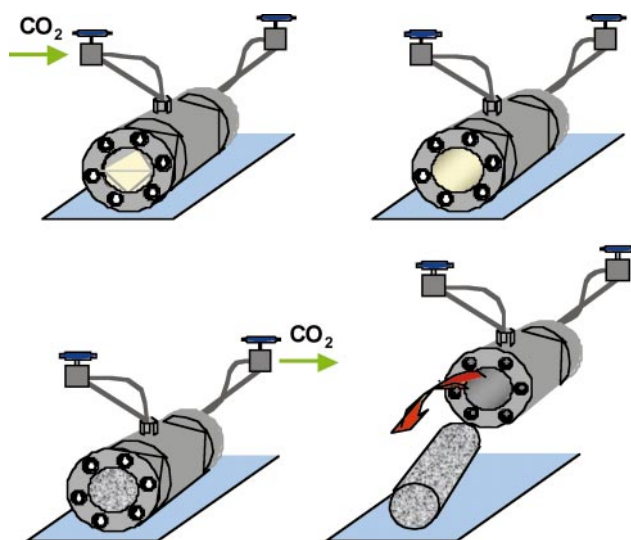
Fig. 9 General method for synthesizing cross-linked porous polymer monoliths in scCO₂. (a) The monomer(s) and initiator are added to a high-pressure view cell which is then filled with liquid CO₂. (b) The reactor is heated to form a homogeneous supercritical solution and to initiate polymerisation. (c) After polymerisation is complete the CO₂ is vented from the reactor. (d) The porous monolith is removed from the vessel. No solvent residues are left in the polymer matrix and the product does not require any further purification. The product conforms to the shape of the reactor, and this method can be applied to the formation of porous monoliths within a range of containment vessels, including chromatography columns and narrow-bore capillaries.

phase separation). After 12 h the CO₂ was vented from the reactor and the polymer removed as a continuous porous monolith which conformed to the shape of the reaction vessel. The pressure could be vented quite rapidly (over a period of a few minutes) and no cracking of the materials was observed. This process differs from the method described by Beckman[152] in that the EDMA- and TRM-based polymers were much more rigid and highly cross-linked: as a consequence, pore growth *via* gas expansion was not a viable mechanism and the pore structure of these materials was not microcellular [see Fig. 8(b)], but rather consisted of a series of interconnected channels between fused particles. The median pore diameters for the samples varied over a very wide range (20–8000 nm) depending on the monomer concentration. In general, higher monomer concentrations led to smaller pores, and this was ascribed to the mechanism of primary particle nucleation and phase separation. Under the appropriate conditions, narrow unimodal pore size distributions could be obtained (Fig. 10). Nitrogen adsorption/desorption analysis (BET method) revealed surface areas of 5–330 m² g⁻¹, depending on the average pore size. Preliminary results indicated that pore sizes could be fine-tuned by varying the CO₂ pressure, thus exploiting the variable density associated with SCF solvents.
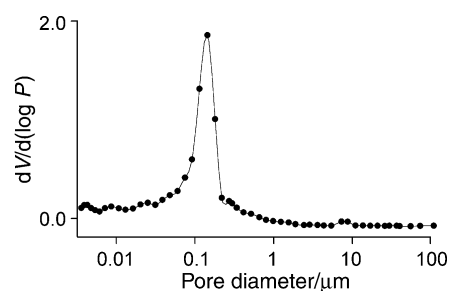

Fig. 10 Pore size distribution for a cross-linked porous polymer synthesized in scCO₂ from monomer **10**, as measured by mercury intrusion porosimetry (50% v/v **10** in scCO₂, 50 °C, 2% w/v AIBN, 310 bar). Median pore size = 100 nm, surface area = 269.4 m² g⁻¹.

It was also shown that pore size distributions could be controlled by "reverse micellar imprinting."[156,157] This involved polymerisation in the presence of an aqueous microemulsion [12.5% v/v water stabilised by sodium bis(2-ethylhexyl) sulfosuccinate (AOT)] which provided a template for pore formation. Interestingly, stable water-in-CO_2 micro-emulsions were formed in the presence of AOT, presumably because of the high concentration of TRM monomer (50% v/v) which acted as a cosolvent. The ease of solvent separation associated with SCFs may favour the use of CO_2 for the formation of macroporous monoliths, particularly in applications where complete removal of the porogenic diluent is important.

Another important example of the synthesis of porous polymers is the direct formation of aerogels by sol–gel polymerisation of alkoxysilanes in $scCO_2$.[158] Sol–gel processing is a useful method for producing amorphous, porous silica and polysilasesquioxane gels,[159] but the commercial applications have been limited by shrinkage (and often cracking) during drying. One of the most successful methods to avoid these problems is drying the gel at a temperature and pressure above the critical point of the solvent, thus eliminating the strong capillary forces associated with air-drying.[160] A common approach has been to form gels in alcohol solvents before exchanging the alcohol for $scCO_2$, which permits drying at lower pressures and much lower temperatures than drying directly from the supercritical alcohol (see Table 1 for the critical properties of some common alcohols). Loy et al.[158] have simplified this procedure by eliminating the organic (alcohol) solvent altogether, and using $scCO_2$ as the sol–gel polymerisation solvent. Standard sol–gel formulations require large quantities of water (typically 2–3 equivalents) for the hydrolysis and condensation of the alkoxysilane monomers. Alcohols are good solvents for these processes because they are capable of mixing water and the non-polar alkoxysilane monomers to give homogeneous solutions. Since the solubility of water in CO_2 is very low, an alternative water-free sol–gel polymerisation method was used.[161] Alkoxysilanes such as tetramethoxysilane (TMOS, 30) or 1,4-bis(triethoxysilyl)benzene (BESP, 31) were polymerised at 35–45 °C in $scCO_2$ (410 bar) in the presence of 13–36 wt% formic acid. Gelation occurred within 12 h and the gel was aged for 12–18 h. At the end of the reaction the CO_2 pressure was released over a 8–18 h period to yield silica aerogels in nearly quantitative yields. Although some signs of cracking and shrinkage were reported, these results are extremely encouraging, particularly because of the relatively short reaction times. Analysis by SEM [see Fig. 8(c)] and TEM revealed the gel structures to be tightly packed aggregates of particles with average pore diameters in the range 40–200 nm. The materials formed from TMOS had surface areas in the range 260–310 $m^2 g^{-1}$ and mean pore diameters of between 31 and 94 Å, while the aerogels formed from BESP had slightly lower mean pore sizes (24–55 Å) and rather higher surface areas (471–586 $m^2 g^{-1}$).

2.6 Bulk condensation polymerisation using CO_2 as a plasticiser

In the polymerisation reactions described in Sections 2.1–2.5, CO_2 has been employed as a solvent for the initiator and monomer (or solely the initiator in the case of inverse emulsion polymerisation). A quite different approach[162] has been to exploit the fact that CO_2 is a good plasticising agent (see Section 1.3) in order to carry out melt phase polycondensation reactions. Many industrial condensation polymerisations are carried out in the melt phase without the use of any organic solvents to produce high molecular weight material. In these systems the reaction is driven by the removal of a small molecule condensate (e.g., water, MeOH, phenol), usually by high vacuum. The cost of implementing and maintaining high vacuum systems on a commercial scale can be considerable.

Furthermore, as high molecular weights are reached, the viscosity of the melt can become very high, thus making stirring and processing more difficult (e.g., the viscosity for poly(4,4'-cyclohexylidene bisphenol) carbonate can reach 10^6 P at 280 °C[163]). The use of $scCO_2$ in melt phase polycondensation has the potential to address both of these problems. Swelling and plasticisation of a polymer melt by CO_2 will tend to produce a significant reduction in viscosity, thus enhancing mobility of both the condensate and the polymer chain ends. Furthermore, if $scCO_2$ is used at densities such that the condensate has appreciable solubility in the fluid, this allows the possibility of supercritical fluid extraction (SFE) as an alternative method for driving the reaction to completion.[164]

Odell and Hamer have described the synthesis of poly-carbonates via melt phase transesterification of diphenyl carbonate with a range of bisphenols [bisphenol A 32, P, AF, and Z].[163] Reaction temperatures were in the range 180–250 °C with CO_2 pressures of 207–241 bar. Under these conditions the density of pure CO_2 is considerably below the critical density ($\rho_c = 0.47$ g cm^{-3}). Temperature and pressure parameters were chosen so as to extract the condensate (phenol) while minimising removal of the diphenyl carbonate starting material. Catalysts such as $Ti(O(CH_2)_3CH_3)_4$, $CH_3(CH_2)_3Sn(=O)OH$, and $[CH_3(CH_2)_3]_4N^+[B(C_6H_5)_4]^-$ were used in this process.

DeSimone has used similar techniques for the synthesis of polycarbonate from bisphenol A and diphenyl carbonate in the presence of $scCO_2$.[165] The catalyst used in these polymerisations was tetraphenylphosphonium tetraphenylborate (TPP-TPB), and it was shown that polycarbonate could be obtained with molecular weights, M_n, as high as 1.3×10^4 g mol^{-1}. Control experiments using a flow of argon instead of extraction with $scCO_2$ led to lower molecular weight products, suggesting that plasticisation by CO_2 and/or solubility of the condensate in the SCF was indeed important. A high-pressure view cell was used to conduct swelling measurements on two polycarbonate samples with number-averaged molecular weights of 2500 and 5000 g mol^{-1} respectively. The swelling behaviour was found to be the same for both samples, and swellings of around 30–55% were observed at 235 °C with CO_2 pressures in the range 125–350 bar.

Melt phase polymerisation in the presence of $scCO_2$ has also been used for the synthesis of poly(ethylene terephthalate) (PET)[166] and nylon-6,6.[167]

2.7 Formation of polymer blends

The use of $scCO_2$ as a solvent for the formation of polymer blends has been studied in some depth, notably by McCarthy and colleagues. The general procedure has been to use $scCO_2$ as a swelling agent in order to infuse or "impregnate" a CO_2-insoluble polymeric host with a mixture of monomer(s) and an initiator. Polymerisation is then initiated thermally within the host polymer to form a blend, either in the presence of $scCO_2$[168] or after venting the CO_2 solution. (This is similar to the method described in Section 2.2 for the preparation of polypyrrole composites,[111] although in that case only the initiator was introduced via SCF impregnation.) Watkins and McCarthy studied the polymerisation of styrene within a range of host polymers, including poly(chlorotrifluoroethylene) (PCTFE), poly(4-methyl-1-pentene) (PMP), polyethylene (PE), bisphenol A polycarbonate, poly(oxymethylene), and nylon-6,6.[169,170] Mass uptakes as high as 118% based on the original mass of the polymer were observed. Differential scanning calorimetry (DSC) revealed a strong glass transition in the modified samples in the temperature range 100–108 °C, indicating the presence of polystyrene. In the case of PCTFE, which was studied in most detail,[170] extraction of the polystyrene phase and subsequent GPC analysis revealed that the polystyrene had high molecular weight ($M_n > 1 \times 10^5$ g mol^{-1}). Little or no

evidence of grafting was observed, and tunnelling electron microscopy (TEM) revealed that the PS existed as discrete, phase-segregated regions throughout the thickness of the PCTFE samples. The synthesis of polystyrene/polyethylene composites,[171] poly(vinyl chloride) (PVC)/poly(methacrylic acid) (PMAA) composites,[172] and poly(tetrafluoroethylene-co-hexafluoropropene) (FEP)/polystyrene blends[173] has been carried out via similar routes. In the latter study, attempts were made to prepare composite foams by saturation of the blends with scCO2 and subsequent rapid depressurisation. This showed only limited success, because at lower temperatures the crystalline domains of FEP prevented expansion, while higher temperatures led to large-scale phase segregation of the blends. Lastly, Rajagopalan and McCarthy have reported the use of scCO2 as a new route to polymer blend formation and surface modification.[174] Three fluoropolymer substrates were studied (PTFE, PCTFE and FEP) using a two-step modification procedure (Fig. 11). In the first step, blends or semi-interpenetrating networks were prepared by carrying out the free-radical polymerisation of styrene (or styrene with divinylbenzene or triallyl cyanurate) within the SCF-swollen polymer substrate. The second step involved sulfonating the polystyrene phase using heterogeneous (solution–solid) conditions. The composition of the surfaces was determined by X-ray photoelectron spectroscopy, and wettability was assessed using water contact angle measurements. Depressed advancing and receding contact angles indicated increased wettability of all of the fluoropolymer samples studied.

In addition to the formation of polymer blends, scCO2 has been used for the generation of metal–polymer composites (Section 3.3) and for grafting reactions (Section 3.4), again via CO2-induced plasticisation and precursor impregnation.

3 Polymer processing using supercritical CO2

3.1 Polymer fractionation

The use of supercritical fluids for the fractionation of polymers is quite well established[175] and only a brief overview will be given here, along with a few recent examples of the use of scCO2 in this area. It should be noted that CO2 is just one of several SCFs that have been used for polymer fractionation.[97b,176] The main techniques for the SCF fractionation of polymers are isothermal decreasing pressure profiling and isothermal increasing pressure profiling.[3,177] Decreasing pres-

sure profiling is easily practised on an industrial scale, while the fractionation of smaller quantities of polymer on a laboratory scale is more readily achieved using an increasing pressure profile. Polymer fractionation by isothermal decreasing pressure profiling involves a sequential reduction in pressure of a SCF–polymer solution, such that narrow molecular weight fractions of the polymer sample are precipitated in a series of collection vessels or "separators" [see Fig. 12(a)]. Conversely, increasing pressure profiling involves the extraction of a polymer sample with a SCF solvent using a sequential (or continuous) increase in the pressure. As the pressure and the solvent density are raised, progressively higher molecular weight material is extracted, thus leading to fractionation [see Fig. 12(b)].[178] A closely related technique is the extraction of low molecular weight oligomers from polymers (Section 3.2). Both fractionation methods described above rely on the variable density associated with SCF solvents. A recent example of the use of increasing density profiling is the fractionation of polyisobutene (PIB) using scCO2.[179a] In this study a PIB sample ($M_n = 1274$ g mol^{-1}, $M_w/M_n = 1.54$) was fractionated at 50 °C. A preliminary extraction was carried out for 10 min using a CO2 density of 0.636 g cm^{-3} (corresponding

Fig. 11 Two-step polymer surface modification. Step (a): the polymer substrate is infused with a monomer and initiator using scCO2 as the swelling agent. Heating causes polymerisation within the swollen polymer host to form a microsegregated blend. Step (b): the nascent polymer phase is chemically modified which leads to a composite material which has surface properties quite different from the original polymer substrate.
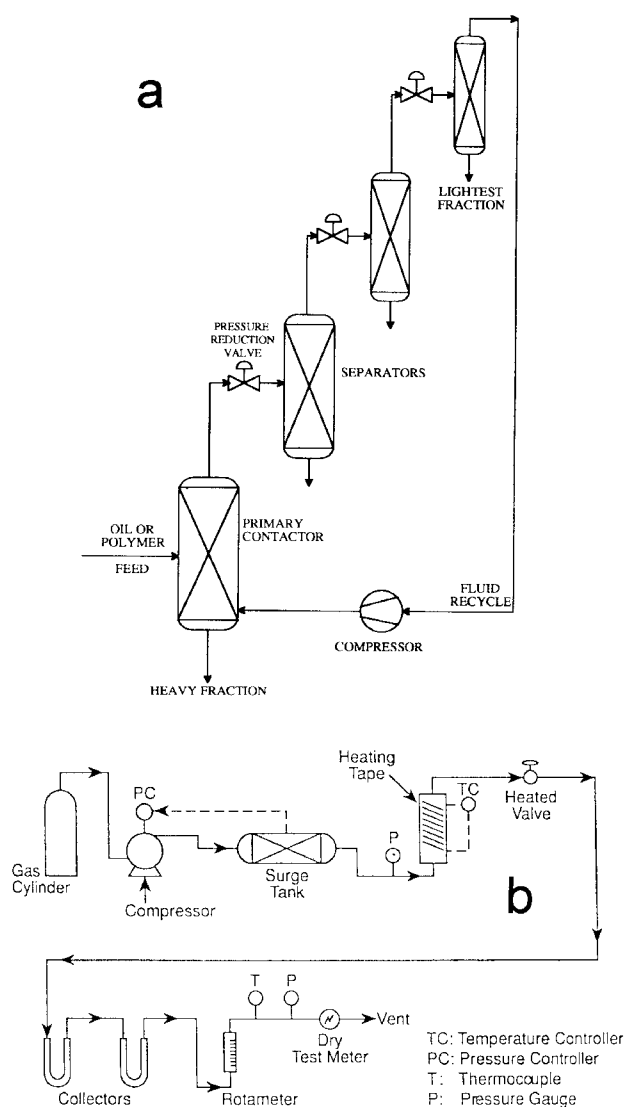

Fig. 12 Apparatus used for polymer fractionation using SCFs. (a) A series of separators used for polymer fractionation by isothermal decreasing pressure profiling. Four separators are shown, but a larger number may be used in practice. (b) Isothermal increasing pressure profiling. Both methods exploit the variable density associated with supercritical fluids. Figures reproduced with permission from ref. 3, copyright Butterworth-Heinemann.

to a pressure of 130 bar) in order to remove the low molecular weight tail. Continuous extraction was then performed at 50 °C with a linear density programme, rising from 0.656 to 1.011 g cm^{-3} at a rate of 6.32×10^{-3} g cm^{-3} min^{-1}. The flow rate of CO_2 was 10 cm^3 min^{-1}. Fig. 13(a) shows the density programme as a function of r, where r is the ratio of the amount of fluid passed to the initial amount of polymer. In addition to the material from the initial extraction, eight further fractions were collected at constant density intervals of 4.5×10^{-2} g cm^{-3} [Fig. 13(b)]. In total, 52% by weight of the PIB sample was extracted. It was shown that the molecular weight distributions of the various fractions were all low [$M_w/M_n = 1.02-1.08$, Fig. 13(c)]. Furthermore, the variation in both the molecular weight and the molecular weight distribution with increasing r values was shown to agree well with theoretical predictions.[179a,b] A PDMS sample ($M_n = 1.28 \times 10^4$ g mol^{-1}, $M_w/M_n = 1.32$) was fractionated by a similar method to give a series of fractions with molecular weight distributions in the range $M_w/M_n = 1.06-1.20$ (84-86% by weight of the PDMS sample extracted). These experiments illustrate the potential of density programming in SFE for the preparation of polymers with low molecular weight distributions for use as analytical standards (*e.g.*, for calibration in size exclusion chromatography).

Another very important method for the separation of oligomers is supercritical fluid chromatography (SFC).[180,181] This has been applied to the fractionation of polymers, both for analytical purposes[182,183] and on a preparative scale.[184-187] As might be expected, CO_2 is especially suited for the fractionation of highly fluorinated polymers which are insoluble in most common organic solvents. Recently, Wu *et al.* used packed capillary column SFC for the separation of perfluorinated polyethers with the general structure $HOCH_2O[(CF_2O)_x-(CF_2CF_2O)_y]CH_2OH$.[188] A fluorocarbon-bonded stationary phase, Fluofix 120N (5 μm and 120 Å), was used as the packing material at various pressures and temperatures. Under the appropriate conditions, approximately 180 per-

fluorinated polyether oligomers were resolved, with average molecular weights ranging from 2000 to 4000 g mol^{-1}. The chromatographic behaviour of the fluorocarbon-bonded stationary phase was compared with octadecyl silica (ODS) particles, and it was shown that the fluorinated packing gave rise to more selective retention under SFC conditions. In separate studies, the fractionation of perfluoropolyether materials using CO_2 was carried out with the purpose of developing CO_2-soluble chelating agents[189] and hard-disk lubricants.[190] Perfluorinated copolymers have also been fractionated by isothermal increasing pressure profiling using supercritical SF_6.[191]

In addition to the use of SFE and SFC, there have been many studies on the fractionation of polymers using polymer–organic solvent phase separation. For an overview of this technique the reader is referred to the text by McHugh and Krukonis.[3] Recently, there has been considerable interest in the use of supercritical antisolvent induced phase separation, both for the formation of polymer particles (Section 3.6) and for the fractionation of polymers. Polymers may be fractionated by the addition of a compressed gas to a solution of a polymer in an organic solvent: this causes a phase split into a polymer-rich phase of high concentration and a polymer-lean phase that contains very little polymer. Bungert *et al.* have employed this method for the fractionation of a model 50 : 50 mixture of two monodisperse polystyrene samples ($M_n = 40 \times 10^3$ and 160×10^3 g mol^{-1} respectively, $M_w/M_n = 1.09$) using a cyclohexane–CO_2 solvent system.[192] Another interesting example of the use of CO_2 for polymer separations is the fractional precipitation of proteins. Winters *et al.*[193] have described the use of CO_2 as an antisolvent for the precipitation of alkaline phosphatase, insulin, lysozyme, ribonuclease, trypsin, and their mixtures from dimethyl sulfoxide (DMSO) solutions. Compressed CO_2 was added continuously and isothermally to stationary DMSO solutions, and dissolution of CO_2 was accompanied by a pronounced volumetric expansion. The solubility of each protein in the CO_2-expanded DMSO was different, illustrating the potential to separate and purify proteins by this method. Similar methods can be used for the production of microparticulate protein powders by antisolvent precipitation.[194]

3.2 Polymer extraction and purification

The extraction of small molecules from polymer matrices is important for two main reasons. First, most commercial polymers contain a range of additives (*e.g.*, plasticisers, antioxidants, UV stabilisers) as well as a host of contaminants (*e.g.*, residual monomer, oligomers, solvent residues). It is important for polymer manufacturers to determine accurately the levels of these various species in their products in order to ensure that the materials are fit for the intended purpose. It is usually necessary to extract compounds quantitatively from the polymer matrix before analysis, traditionally by solvent-intensive methods such as Soxhlet extraction or the polymer dissolution method. The second reason for carrying out polymer extraction is for purification, either to meet regulatory requirements (*e.g.*, for biomedical materials) or to improve the physical properties of the polymer in some way. In addition to reductions in organic solvent usage, supercritical fluid extraction (SFE) has many advantages over Soxhlet extraction, including shorter extraction times, adjustable solvent strength, and the ability to make on-line analyses.[3,195] Furthermore, the extraction temperature in SFE can be varied continuously from the critical point of the SCF to temperatures above the glass transition temperature of the polymer. By contrast, Soxhlet extraction is limited by the boiling point of the extraction solvent. The low critical temperature of CO_2 (31.1 °C) makes

Fig. 13 (a) Density ramp used for the separation of a polyisobutene sample using scCO$_2$. (b) Variation in molecular weight of nine fractions collected at increasing solvent densities. (c) Variation in molecular weight distribution, P, of the fractions (M_w/M_n for the original PIB sample = 1.54). r = Ratio of the amount of fluid passed to the initial amount of polymer. Reprinted from ref. 179(*a*), copyright (1998), with permission from Elsevier Science.

it an excellent solvent choice for the extraction of thermally labile compounds under moderate conditions.

In general, the key factors in SFE are solubility of the extract in the fluid, the rate of mass transfer out of the matrix, and the elution rate.[196] Mass transfer occurs *via* diffusion from the polymer matrix to the polymer–SCF interface, where dissolution in the SCF can occur.[197] Diffusion through the matrix will usually be slow compared to diffusion from the polymer–SCF interface into the bulk solvent because of the high solute diffusivities associated with SCFs. Thus, the rate-limiting step in SFE will tend to be either diffusion through the polymer matrix or elution out of the extraction vessel (Fig. 14). If the rate-limiting step is diffusion of the solute in the polymer matrix [Fig. 14(a)] then increasing the diffusion coefficient of the solute will increase the extraction rate. The most obvious way to do this is by increasing the extraction temperature. SCF-induced plasticisation will also tend greatly to enhance diffusion rates, particularly if plasticisation lowers the T_g for the polymer below the extraction temperature.[196,198] If the rate-limiting step is elution of the components out of the extraction cell [Fig. 14(b)] then extraction rates can be enhanced by either increasing the solvent strength (*i.e.*, by increasing the extraction pressure or adding a modifier), or by increasing the SCF flow rate. At low temperatures and high pressures (*i.e.*, high solvent densities) solubilities are high but diffusion in the polymer matrix is relatively slow, particularly for crystalline polymers that are not strongly plasticised by the SCF. Conversely, at high temperatures (*i.e.*, low solvent densities) diffusion of solutes in the polymer matrix is fast, but the solubility of components in the SCF may be low, and thus solubility can become the rate limiting parameter. In many systems a compromise will exist between these two extremes, depending on the precise nature of the polymer and the solute. Supercritical CO$_2$ has been used for the extraction and analysis of polymer additives,[199,200] the extraction of monomers[201] and oligomers,[202,203] and the removal of residual solvent from polymer foams.[204] Most of these methods have employed either neat CO$_2$ or CO$_2$ modified with a polar species (*e.g.*, MeOH): however, not all compounds are readily extracted under such conditions. For example, Zacharia *et al.* have reported the use of liquid CO$_2$ for the extraction of PMMA samples which had been doped with 0.16 wt% copper(II) naphthenate.[205] A chelating agent, thenoyltrifluoroacetone, was used to solubilise the copper species in CO$_2$, and it was found that extraction of the metal complex led to a significant improvement in the

thermal stability of the polymer. In principle, one might also use SFE to purify polymers which have been synthesized in scCO$_2$, possibly using the same vessel which was used for the polymerisation reaction. This could be important for the removal of residual monomer or recovery of the stabiliser in dispersion polymerisation.[117]

3.3 Polymer impregnation and dyeing

The same properties that make scCO$_2$ such a useful solvent for extraction have been exploited in the impregnation and dyeing of polymeric materials. In addition to the formation of polymer blends (see Section 2.7), CO$_2$ has been used as a solvent for the introduction of various dyes and metal complexes into polymer hosts. This section focuses on the materials applications of these methods: further general details can be found in the comprehensive review by Kazarian,[2c] which also discusses the technique of supercritical drying. More examples may be found in the review by Sahle-Demessie *et al.*[206] which covers the use of scCO$_2$ for the impregnation of porous solids such as wood.[207]

The replacement of aqueous dyeing solvents with CO$_2$ has great potential for the reduction of waste streams in the textile industry.[208] A particularly attractive technique is disperse SCF dyeing using dyes which have very low solubility in scCO$_2$. For example, West *et al.* have reported SCF dyeing of PMMA films with two azo-dyes; 4-(diethylamino)-4′-nitro-azobenzene **67** and disperse red 1 **68**.[209] *In situ* UV spectroscopy was used to determine the equilibrium solubility of both dyes in scCO$_2$ at 40 °C as a function of pressure. At pressures of around 200 bar the equilibrium mole fraction of the dyes in CO$_2$ was found to be very low ($\approx 1 \times 10^{-5}$ for dye **67**, $\approx 1 \times 10^{-6}$ for dye **68**). However, partitioning of these dyes between PMMA and the fluid phase was measured, and it was shown that the partition coefficients were large ($K_c = 10^4$–10^5, where K_c is defined as the saturation concentration of the dye in the polymer phase divided by the saturation concentration of the dye in the fluid phase). Thus, appreciable quantities of dye (0.5 wt%) could be loaded into PMMA due to the preferential affinity of the compound for the polymer, particularly in the case of dye **68** (Fig. 15).[210,211]

67 (R = H)
68 (R = OH)

Fig. 15 Photographs of PMMA films dyed using scCO$_2$ as the solvent: (a) Native PMMA film; (b) PMMA film dyed with compound **68**; (c) PMMA film dyed with ferrocene. Note that **68** has very low solubility in scCO$_2$ ($\approx 1 \times 10^{-6}$ M) and dyeing occurs because the partition coefficient between the polymer phase and the SCF is very high ($K_c = 10^4$–10^5, see text). A dye concentration of 0.5 wt% can be achieved in the PMMA matrix. By contrast, ferrocene is very soluble in scCO$_2$ (≈ 20 wt% at 55 °C, 345 bar),[3] which illustrates how CO$_2$ is a useful solvent for the introduction of a wide variety of species into polymer substrates. Reproduced with permission from ref. 211(b), copyright International Scientific Communications, Inc.
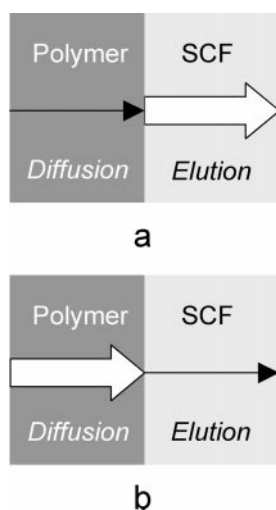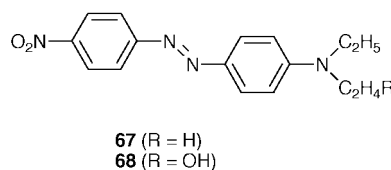
Fig. 14 Schematic representation of the two possible extremes concerning the rate-limiting step in SFE. (a) Rate of extraction is limited by diffusion through the polymer matrix. (b) Rate of extraction is limited by diffusion from the polymer–SCF interface into the bulk SCF. In the case of scCO$_2$ the rate of diffusion in the polymer may be greatly enhanced by polymer plasticisation. Redrawn from ref. 198(*b*).
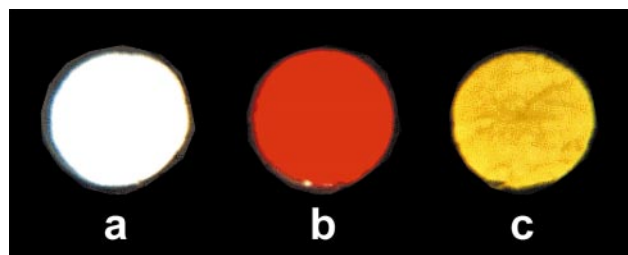
Since very little dye is actually dissolved in the fluid at any given time, this minimises dye loss and hence environmental burdens. Other studies have centred on the SCF dyeing of PET[212,213] and cellulose diacetate[213] fibres, whereas Ma and Tomasko have studied the use of scCO$_2$ for the coating and impregnation of fibrous polyethylene with a non-ionic surfactant.[214] An interesting technique was described by Barry and Soane, who investigated second harmonic generation in thin polymer films processed with CO$_2$.[215] In their studies thin polycarbonate films were cast containing **68**, and then swollen with CO$_2$. It was found that plasticisation of the polymer matrix allowed the alignment (or poling) of compound **68** in an electric field, and second harmonic generation was observed. The traditional method for poling dye–polymer systems involves heating the polymer above its T_g and then applying an electric field to the system. The poling of CO$_2$-plasticised materials could allow the use of thermally labile dyes, and this approach might lead to the development of novel advanced non-linear optical components.

69
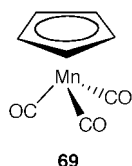
Several research groups have investigated the use of scCO$_2$ for the introduction of metal complexes into polymers. Howdle *et al.* studied the impregnation of a transition metal carbonyl complex (**69**) into low- and high-density polyethylene films and powders.[216] It was shown that a range of spectroscopic techniques was required fully to characterise the distribution of the complex throughout the polymer matrix.[216,217] Techniques such as FT-Raman, diffuse reflectance IR, and photo-acoustic IR spectroscopy were used to distinguish between surface-coated organometallic and material that was impregnated in the bulk polymer. This is particularly important (and difficult) in the case of impregnated polymer powders. Poliakoff and co-workers have studied thermal and photo-chemical reactions of organometallics within polymer matrices, where scCO$_2$ was used to dope the organometallic species.[218] The key advantage of using CO$_2$ in these systems is that no solvent residues are left in the polymer which might otherwise interfere with the subsequent reaction chemistry. Popov *et al.* have reported the modification of the tribological properties of an aromatic polyester *via* impregnation with copper(II) hexafluoroacetylacetonate using scCO$_2$ as the impregnation solvent.[219] Significant changes in surface morphology, internal structure, and chemical composition of the polymer were observed after thermal treatment at 230 °C for 2 h to decompose the impregnated copper complex. Nanodisperse copper oxide was detected in the polymer matrix, and wear tests showed improved tribological properties for the modified materials. The formation of polymer–metal nanocomposite materials was also reported by Watkins and McCarthy.[220] In their system, nanoscale platinum clusters were formed within two different host polymers [poly(4-methyl-1-pentene) (PMP) and PTFE] *via* reduction of a metal precursor (**70**). Polymer samples were impregnated with precursor **70** using scCO$_2$ (80 °C, 155 bar, 4 h) prior to reduction either by autocatalytic hydrogenolysis (Scheme 3) or by thermolysis at 230 °C. Platinum contents of 1.8–2.0% w/w were found for the samples, and TEM imaging revealed that the composites consisted of discrete platinum nanoclusters with diameters in the range 10–100 nm (Fig. 16). The distribution of metal and the size of the individual clusters within the polymer matrix could be controlled by adjusting the experimental parameters. In particular, homogeneous modifications could be achieved by
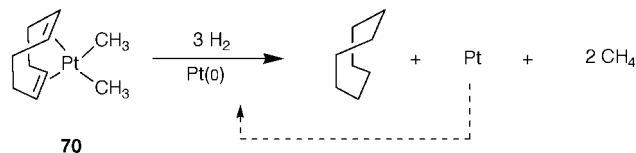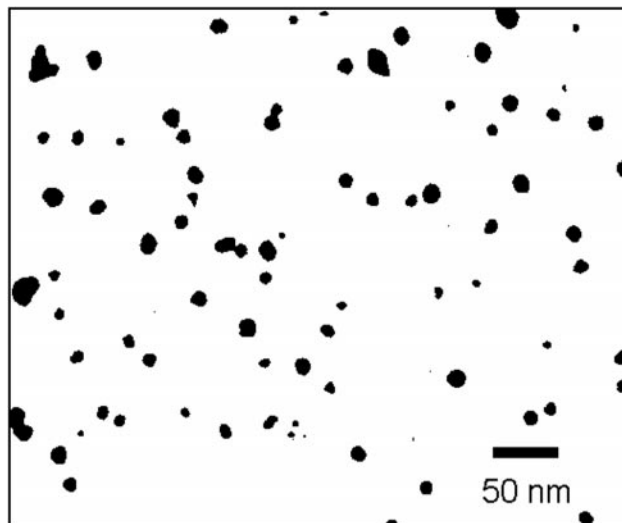
Scheme 3

Fig. 16 TEM image of platinum nanoparticles deposited in a PMP sample *via* impregnation of compound **70** using scCO$_2$ followed by reduction by hydrogenolysis (see Scheme 3). After reduction, the nanocomposite material was deep black with a silvery hue. Reproduced with permission from ref. 220, copyright American Chemical Society.

allowing the SCF solution to equilibrate with the swollen polymer before reduction, whereas surface-selective depositions were obtained under conditions where the rate of precursor absorption was low compared with the reduction rate.

3.4 Heterogeneous chemical modification of polymers

Since CO$_2$ is a good solvent for the impregnation of polymers with low molecular weight dopants, one might envisage the use of these methods to carry out heterogeneous chemical modifications on polymer substrates, particularly if the reactions occur under conditions where the polymer is swollen and plasticised by CO$_2$. This has been demonstrated in a few systems, although the number of examples is as yet fairly small. Yalpani has studied the chemical modification of polymers and biopolymers such as chitosan, amylose, and poly(vinyl alcohol) (PVA) using scCO$_2$ as the solvent.[221] For example, an aqueous dispersion of chitosan powder and glucose was allowed to react in the presence of scCO$_2$ (27.4–31.4 bar, 60 °C, 1.5 h) to give almost complete conversion into the chitosan glutimine derivative. A very high degree of substitution was obtained ($\approx$90%), even though the reactions were found to be slow under conventional conditions. The reason for the enhanced reactivity under supercritical conditions was not entirely clear, although a number of possibilities were considered. The oxidation of polymers such as starch and PVA was also investigated using mixtures of scCO$_2$ and O$_2$, thus taking advantage of the high solubility of gaseous reagents in SCF solvents. Hayes and McCarthy have studied the free-radical grafting of maleic anhydride (MAH) onto PMP using scCO$_2$ as solvent and swelling agent.[222] Reactions were conducted using either benzoyl peroxide (BPO) or dicumyl peroxide (DCP) initiators at 125 °C under pressures of 400–430 bar. DCP was found to be the more effective initiator, and maleations as high as 7 mol% could be achieved after a 5 h reaction period. The primary advantage of using scCO$_2$ to conduct maleations was

the ability to control the degree of maleation in bulk samples without the need for either solution processing or efficient extruder mixing. Similarly, supercritical propane has been evaluated as a swelling solvent for the modification of MAH-grafted high-density polyethylene with diamines:[223] presumably, the reactivity of primary amines with CO_2 might preclude its use in this particular application. The use of gamma irradiation for the modification of low-density polyethylene in the presence of $scCO_2$ was investigated by Spadaro and colleagues, who showed that carboxylation of the polymer occurred under the conditions used (e.g., 38 °C, 150 bar, absorbed irradiation doses = 250–650 kGy at a dose rate of 0.57 kGy h^{-1}).[224] The carboxylation reaction was accompanied by cross-linking, as demonstrated by the significant gel fractions in the irradiated polymers (up to 75%).[225] The grafting of MAH onto isotactic polypropylene via gamma irradiation using $scCO_2$ as a swelling agent has also been investigated.[226] Finally, Yarita et al. have developed a method for end-capping octadecylsilyl (ODS) silica gels using $scCO_2$ as a silylation medium.[227] The effects of temperature and pressure on the deactivation of the gels were investigated, and HPLC (or SFC) evaluation of the resulting materials indicated that the most inert gels were obtained via silylation at 180 °C and 245 bar. It was found that commercially available end-capped ODS-silica gels could be further deactivated by this technique.

3.5 Microcellular materials

In addition to the formation of microcellular polymer foams via polymerisation in $scCO_2$[152,153] (see Section 2.5), a number of research groups have investigated the use of $scCO_2$ as a foaming agent for non-reactive processing. Microcellular polymers (i.e., polymers with cell sizes less than or equal to 10 μm) are used as separation media, adsorbents, controlled release devices, biomedical devices, and as lightweight structural materials. Traditional methods for the formation of these materials are based on a temperature quench (or, less commonly, the addition of an antisolvent) to induce phase separation of a homogeneous polymer solution.[228] Thermally induced phase separation involves dissolving the polymer in an appropriate hydrocarbon solvent and quenching the temperature to induce phase separation. This is followed by solvent removal, either by freeze-drying or by SFE. Beckman has developed an alternative "solvent free" approach, whereby a polymer is saturated with $scCO_2$ at moderately elevated temperatures followed by rapid depressurisation at constant temperature (i.e., a pressure quench as opposed to a temperature quench). This method takes advantage of the large depression in T_g found for many polymers in the presence of CO_2 (see Section 1.3), which means that the polymer may be kept in the liquid state at relatively low temperatures. By lowering the pressure at a fixed temperature the amount of diluent absorbed by the polymer is decreased. Thus, T_g begins to rise, eventually to the point where T_g for the polymer is higher than the foaming temperature: at this point the cellular structure can grow no further and is locked in. The sudden reduction in pressure leads to the generation of nuclei due to supersaturation, and these nuclei grow to form the cellular structure until vitrification occurs. This method has been used for the generation of PMMA foams consisting of a microcellular core surrounded by a relatively non-porous skin (see Fig. 17).[229] The cell structures formed had narrow cell size distributions, with polydispersity indices in the range 1.3–1.7. Average cell sizes were found to vary from 0.5 to 3.0 μm, depending on the saturation time. Further studies[230] on the formation of microcellular PMMA foams via this route showed that the properties of the foams could be tailored by changing saturation pressures and saturation times. A theoretical model for cell nucleation and growth was also presented.[231] A similar approach was taken by McCarthy and colleagues, who have
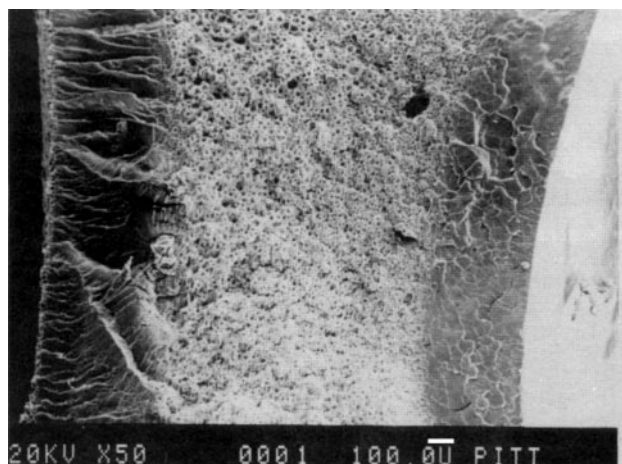
Fig. 17 Typical foam structure generated by pressure induced phase separation in a PMMA–$scCO_2$ solution (saturation pressure = 170 bar, 40 °C, 24 h). The material is characterised by an integral structure with a microporous core and a non-porous skin. One of the advantages of this method is that foaming can occur at low temperatures due to CO_2-induced plasticisation. Reproduced with permission from ref. 229, copyright RAPRA Technology Limited.

studied the formation of microcellular polystyrene foams using $scCO_2$.[232] The long-term goal of this research is the synthesis of composite microcellular materials. It was found that an equilibrium mass uptake of 11.8% CO_2 was adsorbed by polystyrene at 80 °C and 240 bar. Bulk foam densities in the range 0.05–0.85 g cm^{-3} were obtained, depending on the foaming temperature. Average cell diameters for these materials varied over a wide range (1–70 μm) depending on experimental conditions such as foaming temperature, saturation pressure, and depressurisation time. Interestingly, anisotropic cell morphologies could be obtained, and the nature and degree of anisotropy was influenced by the shape of the pressure vessel and the magnitude of the pressure drop. The compressive behaviour of PS foams prepared by this method was also investigated, and it was found that the yield stress for the foams depended on the size, shape, and orientation of the cells.[233] More recently, the pressure quench method has been extended to the generation of microcellular polypropylene[234] and poly(styrene-co-acrylonitrile) (SAN)[235] foams.

3.6 Polymer particle formation

The use of supercritical fluids for the formation of particles is a broad area of research. Discussion in this section will be confined to the generation of polymer particles using supercritical CO_2: techniques such as the processing of pharmaceutical compounds[236] semiconductor precursors,[237] and organometallic complexes[7a,238] will not be discussed here, nor will the use of other supercritical fluids.[239] Carbon dioxide has many advantages as a solvent for polymer particle formation, especially for controlled release applications where the elimination of toxic solvent residues is of key importance.

There are several techniques for the preparation of polymer particles using SCFs but these can be divided into two main categories: those which involve precipitation from a homogeneous supercritical solution by rapid expansion, and those which use the SCF as an antisolvent. Because of the profusion of acronyms and terminology in this field, a brief summary is given here (see Table 3). The process of particle formation by rapid expansion of a supercritical fluid (RESS) begins with a homogeneous solution of a compound in a SCF (or a SCF containing a cosolvent) which is then expanded rapidly to form precipitated particles. This technique requires that the compound has reasonable solubility in the SCF, and thus the preparation of polymer particles using rapid expansion of

Technique	Acronym	Ref.
Rapid Expansion from Supercritical Solution	RESS	242–249
Gas Antisolvent Precipitation	GAS	240
Supercritical Antisolvent Precipitation	SAS	240,245,258,259
Precipitation by Compressed Antisolvent	PCA	240,253–255,260–264
Aerosol Solvent Extraction System	ASES	240,250–252
Solution Enhanced Dispersion by Supercritical Fluids	SEDS	240,256,257

$scCO_2$ has been limited so far to a relatively narrow range of CO_2-soluble materials. Supercritical antisolvent micronisation exploits the *lack* of solubility of the starting material in the SCF, and the use of $scCO_2$ is therefore more widely applicable in the case of polymer processing. The technique of GAS (gas antisolvent) involves the injection of CO_2 into an organic solvent, just as one might add a conventional liquid antisolvent. The other antisolvent techniques are referred to variously as SAS (supercritical antisolvent), PCA (precipitation by compressed antisolvent), ASES (aerosol solvent extraction system) and SEDS (solution enhanced dispersion by supercritical fluids). In contrast to GAS where CO_2 is added to the organic solution, these techniques involve injecting an organic solution into dense CO_2 or, alternatively, co-injecting the organic solution and CO_2 into a common vessel. This may be carried out either in a batch mode or as a continuous process. Although these processes differ in important ways, the fundamental principle behind all of these methods is essentially the same: CO_2 is a poor solvent for the compound in the organic solution and thus precipitation occurs upon mixing. The design of the apparatus, particularly the injection nozzle, can have a profound influence on the resulting product morphology, both in RESS and in antisolvent processes. Further details on SCF antisolvent precipitation can be found in the recent review by Reverchon,[240] while Subra and Jestin[241] provide a more general summary of the advantages of SCFs for the formation of powdered materials in comparison with conventional routes. The fundamentals and applications of RESS have been reviewed extensively by Debenedetti.[242]

The formation of polymer particles using $scCO_2$ *via* RESS is limited by the low solubility of most polymers in this fluid. However, as might be expected, CO_2 is a good solvent for the processing of certain CO_2-soluble fluoropolymers by this route. Mawson *et al.* have studied the preparation of submicron particles [Fig. 18(a)] and fibres [Fig. 18(b)] of a crystalline fluoropolymer, **71**, by rapid expansion from $scCO_2$ solutions.[243] The polymer was processed by spraying a solution of **71** (0.5–2.0 wt%) through an orifice (30 or 50 μm diameter) at pre-expansion temperatures in the range 45–105 °C. This procedure produced 0.3–50 μm particles or 0.3–2.0 μm fibres, depending on the conditions: no evidence was seen for mixed particle–fibre morphologies. The particle size and morphology was found to be influenced by the pre-expansion temperature and, critically, the location of phase separation in the nozzle. As a consequence of this, the length to diameter ratio ($L:D$) of the nozzle was a very important variable. Although most non-fluorinated polymers have very low solubility in CO_2, there are a number of reports on the preparation of poly(lactic acid) (PLA, **72**) and poly(glycolic acid) (PGA, **73**) microparticles by rapid expansion from $scCO_2$ solutions. Tom and Debenedetti showed that irregular sized poly(D,L-lactic acid) particles could be formed by RESS, with particle sizes in the range 10–20 μm.[244] Nucleation of poly(L-lactic acid) from CO_2 (and CO_2–acetone mixtures) produced microparticles and microspheres (4–25 μm), while nucleation of PGA from $scCO_2$ produced both regular-sized particles and also needles 10–40 μm in length. The solubility of polymers **72** and **73** in CO_2 is low, but evidently high enough to allow processing of these materials by RESS. The total solubility of commercial poly(L-
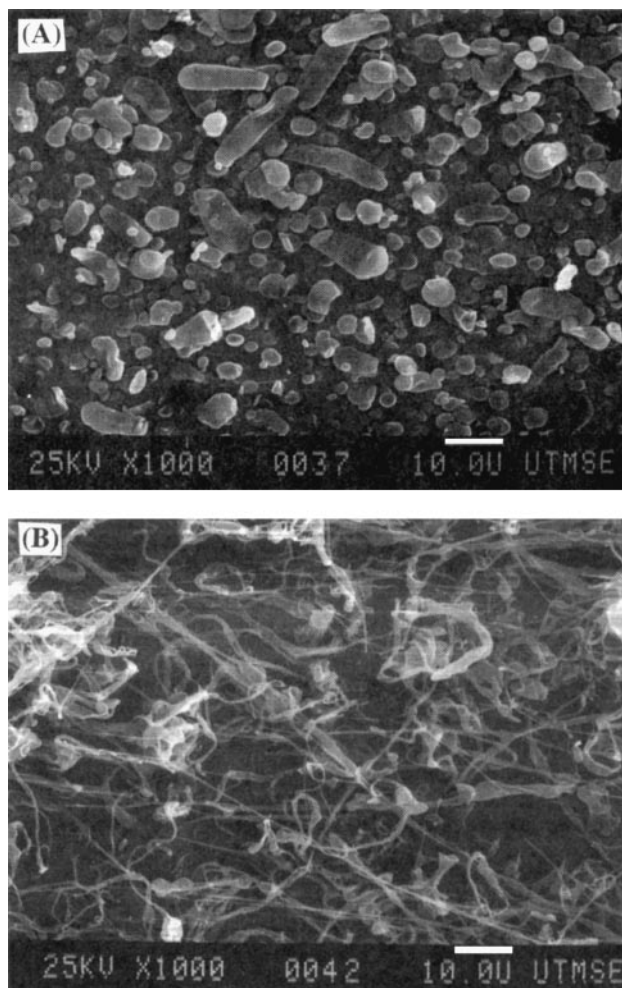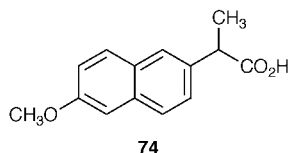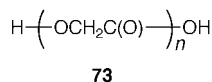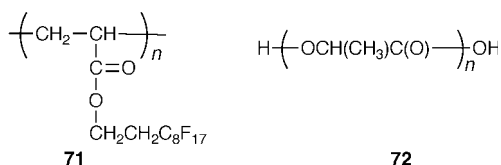

Fig. 18 SEM images illustrating the control of product morphology using RESS (scale bar = 10 μm in both images). (a) Particles of polymer **71** produced by rapid expansion from $scCO_2$ (0.5 wt% **71** in CO_2, pre-expansion temperature = 105 °C, nozzle diameter = 30 μm). (b) Sub-micron fibres of polymer **71** produced by rapid expansion from $scCO_2$ (0.5 wt% **71** in CO_2, pre-expansion temperature = 85 °C, nozzle diameter = 50 μm). A range of product morphologies could be obtained by controlling experimental variables such as the pressure, pre-expansion temperature, concentration, nozzle diameter, and the length-to-diameter ratio ($L:D$) of the nozzle. Reproduced with permission from ref. 243, copyright American Chemical Society.

lactic acid) in $scCO_2$ at 250 bar and 55 °C was ≤0.1 wt%, although the use of acetone (1 wt% in CO_2) as a cosolvent increased this solubility by approximately 500%.[244] The use of $scCO_2$ for the production of micronic particles of a biocompatible polysaccharide has also been investigated, both by RESS and SAS,[245] while Mishima *et al.* have reported the preparation of polyethylene glycol and polyoxyalkylenealkylphenyl ether microspheres *via* rapid expansion from ethanol-modified CO_2.[246] Polymers such as **72** and **73** are useful for the controlled release of drugs, and RESS has been used for the preparation of materials for drug delivery.[247] A systematic study was made on the formation of poly(L-lactic acid) particles and composite poly(L-lactic acid)–pyrene particles by RESS

$$\left[CH_2-CH\right]_n \quad \underset{\substack{C=O \\ | \\ O \\ | \\ CH_2CH_2C_8F_{17}}}{}$$

71

$$H\left[OCH(CH_3)C(O)\right]_n OH$$

72

$$H\left[OCH_2C(O)\right]_n OH$$

73

(structure of naproxen: 6-methoxy-α-methyl-2-naphthaleneacetic acid, bearing CH$_3$, CO$_2$H, and CH$_3$O substituents)

74

using scCO$_2$ modified with CHClF$_2$.[248] Pyrene was chosen as a model non-polymeric solute because it could easily be detected by fluorescence. Three key process variables were explored in detail: the $L:D$ ratio of the expansion device, the pre-expansion temperature, and the solvent composition. In experiments involving the coprecipitation of PLA with pyrene it was found that the pyrene molecules were distributed uniformly throughout the polymer microspheres. Kim *et al.* have reported the microencapsulation of a pharmaceutical molecule, 6-methoxy-α-methyl-2-naphthaleneacetic acid (naproxen, **74**) in poly(L-lactic acid) microparticles by RESS using unmodified scCO$_2$.[249] When PLA was coprecipitated with **74**, microspheres (10–90 μm) loaded with naproxen and some free naproxen (1–5 μm) were observed at a pre-expansion temperature of 90 °C and an extraction pressure of 170 bar (Fig. 19). By using reflected light and fluorescence confocal laser scanning microscopy it was shown that the composite particles consisted of a naproxen core surrounded by a thin polymer coating.

The preparation of drug-loaded microparticles using scCO$_2$ has also been achieved using antisolvent precipitation techniques. Bleick and Müller have investigated the microencapsulation of drugs in poly(L-lactic acid) using the aerosol solvent extraction system (ASES) process.[250] Solutions of polymer and drug in methylene chloride were sprayed into scCO$_2$ under two different conditions: 40 °C/90 bar and 40 °C/200 bar. The
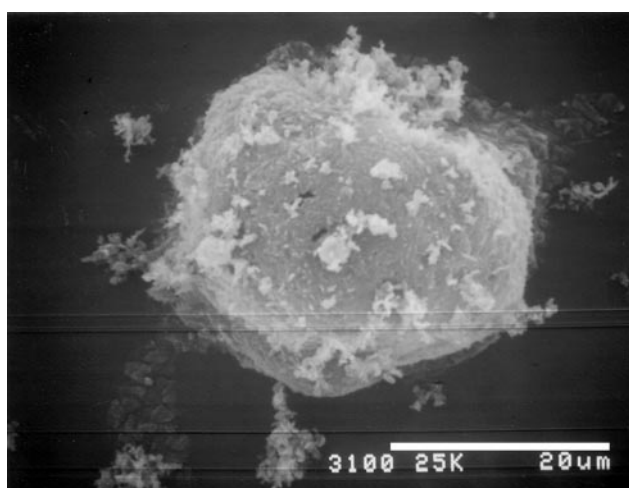

Fig. 19 SEM image of a PLA microsphere loaded with naproxen **74** *via* coprecipitation by RESS (scale bar = 20 μm). Extraction pressure = 170 bar, pre-expansion temperature = 90 °C, length-to-diameter ratio ($L:D$) of the nozzle = 200:1. The PLA particle is approximately 25 μm in diameter with naproxen microparticles (2–5 μm) attached to/ imbedded in the matrix. The product morphology could be controlled by varying the experimental conditions. Reproduced with permission from ref. 249, copyright American Chemical Society and American Institute of Chemical Engineers.

density of the CO$_2$ phase varied from about 0.46 to approximately 0.84 g cm^{-3} over this pressure range. Due to the miscibility of the organic solvent with the SCF, precipitated microparticles with residual levels of organic solvent of less than 30 ppm were formed. Drugs such as piroxicam, indomethacin, hyoscine butyl bromide, and thymopentin were encapsulated, and it was found that the production conditions had to be optimised for each individual drug–polymer combination. Totally non-polar drugs tended to be co-extracted with the organic solvent, while polar drugs were easily encapsulated by this method. Other studies by the Müller group have focused in more detail on controlling the size and morphology of biodegradable microparticles produced *via* the ASES process.[251,252] Falk *et al.* have investigated the preparation of poly(L-lactic acid) microspheres containing pharmaceutical agents such as gentamycin, naloxone, and naltrexone *via* PCA.[253] The drugs were solubilised in methylene chloride using hydrophobic ion pairing to replace polar counter ions stoichiometrically with an anionic detergent, AOT. This solution was then pumped co-currently at a volumetric ratio of 20:1 CO$_2$:solvent through an ultrasonic spray nozzle vibrating at 120 kHz. The drug–polymer composite particles so formed were spherical in shape with diameters in the range 0.2–1.0 μm. *In vitro* release studies for these materials showed minimum burst effects, and the release kinetics was approximately linear with the square root of time, indicating maximum diffusion control of drug release. Efforts were also made to find conditions which optimise residual solvent removal in this process.[254] PCA has also been used for the encapsulation of lysozyme in biodegradable polymers such as poly(L-lactic acid) and poly(D,L-lactic acid-co-glycolic acid),[255] while the preparation of a range of biodegradable microparticles has been achieved by the use of the SEDS technique.[256] The use of SEDS for the processing of biopolymers may prove particularly useful because the biomolecules can be maintained in an aqueous solution prior to particle formation and SFE of the aqueous phase, thus reducing the probability of denaturation.[257]

In addition to the formation of biodegradable polymer particles, a range of other polymeric materials has been processed using scCO$_2$ as the antisolvent. Yeo *et al.* investigated the use of SAS for the preparation of microparticles and fibres of substituted *para*-linked aromatic polyamides *via* precipitation from solutions in solvents such as dimethyl sulfoxide and dimethylformamide.[258,259] Heater and Tomasko used PCA for the processing of epoxy resins, both with and without the use of surfactants in the liquid phase.[260] Johnston and colleagues have published a series of papers on the formation of polymer microparticles by PCA, including polymers such as polystyrene,[261–263] poly(L-lactic acid),[263] and PMMA.[264] In some cases, unusual particle morphologies such as microcellular polystyrene microspheres and microballoons (hollow microspheres) could be obtained, depending on the conditions (Fig. 20).[262] A particularly interesting study involved the formation of polystyrene and PMMA microparticles by PCA in the presence of surfactants similar to those used for dispersion polymerisation in scCO$_2$ (Section 2.1).[264a] It was shown that these stabilisers could minimise particle flocculation by steric stabilisation, especially in the case of PS-b-PFOA **49** surfactants. A subsequent report showed that certain non-fluorinated stabilisers had similar effects on particle morphologies.[264b]

A quite different approach to the formation of polymer particles is the Vedoc Advanced Materials Process or "VAMP$^{\circledR}$" which was recently commercialised by Ferro Corporation (Cleveland, OH).[265] This method can be applied to the processing of a range of composite materials, particularly polymer–pigment formulations for use as powder coatings. Very simply, VAMP$^{\circledR}$ involves the addition of a polymer and a pigment to an autoclave. Supercritical CO$_2$ is then added to the vessel, thus causing the polymer to swell. A stirrer mixes the
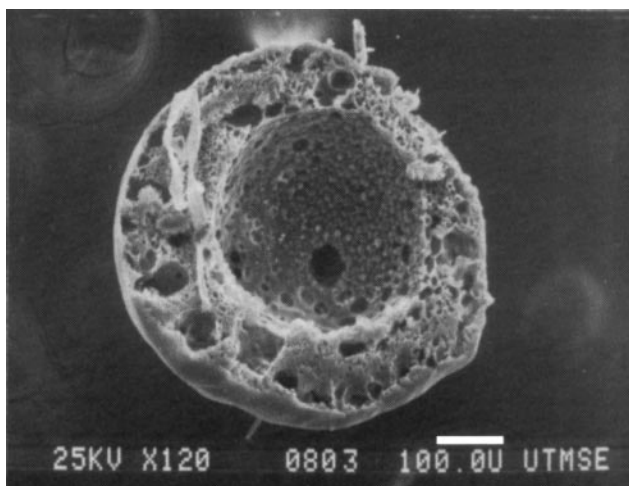
Fig. 20 SEM image of a fractured polystyrene microsphere formed by PCA (scale bar = 100 μm). This sample was produced by spraying a solution of polystyrene (12.8% in toluene) into CO_2 at 22 °C and 70 bar. It consisted of hollow microspheres with 120–150 μm thick shells. Under these conditions the shells were found to be porous with pore sizes in the range 1–100 μm. Reproduced with permission from ref. 262, copyright Butterworth-Heinemann Ltd.

polymer–pigment mixture in order to distribute the pigment particles throughout the plasticised polymer: neither the polymer nor the pigment is soluble in CO_2 under these conditions. The density of the CO_2 phase may also be controlled such that it is as close as possible to the density of the suspended molten polymer. Once a homogeneously mixed system is obtained the vessel is either rapidly depressurised through an orifice to produce particles, or depressurised more slowly to produce a polymer "sponge". In both cases the pigment is distributed uniformly throughout the polymer matrix. The primary advantage of this process is that mixing can occur at low temperatures because the polymer is highly plasticised. In the case of powder coatings formulations this avoids premature curing of the resin, which can be a major problem in conventional melt-extrusion mixing techniques. As in the case of diperse dyeing,[208–211] loss of the pigment is avoided because it is practically insoluble in CO_2. Weidner et al.[266] have described a similar process for the manufacture of powder coatings, the main difference being that their method operates continuously rather than in a batch mode. These processing techniques may prove extremely useful for the preparation of polymer composites containing a range of thermally sensitive components, although presumably the method might be limited to relatively low-melting polymers which are strongly plasticised by CO_2.

3.7 Coatings and lithography

There has been much interest in the use of CO_2 as a solvent for the reduction of volatile organic compound (VOC) emissions during spray coating. The UNICARB system, developed by Union Carbide, uses scCO$_2$ to replace some of the organic solvents which are used in conventional spray coating systems.[267,268] In this process scCO$_2$ is used to replace the volatile organic solvent fraction that is used to obtain atomisation viscosity. Reductions in VOC emissions of 30–70% are claimed, while continuing to use high molecular weight polymer systems that give superior coating performance. The system can produce fine droplet sizes and a "feathered" spray that resembles an air spray but without the high air volume. The technology is applicable to most spray-applied coatings, and has been demonstrated using acrylics, polyesters, cellulosics, alkyds, and commercial paints and lacquers in clear, pigmented, and metallic systems. Likewise, DeSimone has investigated the use of scCO$_2$ as a solvent for the spray coating of stone materials with protective fluorocarbon coatings, in this case without the use of any organic cosolvents.[269]

In addition to spray coating there has been interest recently in the use of CO_2 as a solvent for microlithography. In traditional resist processing, radiation-induced solubility changes are patterned onto a polymer film, followed by treatment with a developer which selectively dissolves either the exposed or the unexposed portion of the film to produce well defined nanostructural features. Current resists are usually developed with an aqueous base: consequently, millions of gallons of waste water from semiconductor processing facilities are treated annually. Supercritical solvents offer the possibility of simpler recycling, and Ober et al. have developed polymer-based resist systems which use scCO$_2$ instead of aqueous developers.[270] Since commercial resists are insoluble in CO_2, a series of fluoropolymer- or siloxane-based imageable copolymers was developed for negative tone development using scCO$_2$. Two types of resist were synthesized (**75a,b**) by the copolymerisation of tert-butyl methacrylate (t-BMA) with either 3-methacryloyloxypropylpentamethyldisiloxane (SiMA) **75a** or pentafluoropropyl methacrylate (PFM) **75b**. These polymers were prepared with both block copolymer and random copolymer morphologies. As would be expected, the solubility of the copolymers in CO_2 increased when the weight fraction of the CO_2-philic comonomer was raised. For compound **75a**, block copolymers containing 57 wt% SiMA ($M_n = 14.9 \times 10^3$ g mol^{-1}, $M_w/M_n = 1.09$) and 70 wt% SiMA ($M_n = 14.9 \times 10^3$ g mol^{-1}, $M_w/M_n = 1.09$) were soluble in CO_2 at 80 °C and 272 bar, whereas the corresponding random copolymers were not. This suggested that the block copolymer morphology was more suitable for this application, and subsequent experiments focused on block copolymer **75a**. Thin films of the polymers (200–350 nm thickness) containing a photoacid generator (triphenylsulfonium hexafluoroantimonate) were spin-coated onto silicon wafers using propylene glycol methyl ether acetate as the solvent. A surfactant, Silwet L-7604, was added to decrease defects in the spin-coated films. After removal of the solvent the samples were imaged using an excimer laser operating at 248.4 nm. This caused cleavage of the tert-butyl groups in the copolymer, leading to a material in the exposed areas of the film which was insoluble in CO_2 (Scheme 4). Development of the image was carried out by SFE,

soluble in CO$_2$ insoluble in CO$_2$

75a [R = CH$_2$CH$_2$Si(CH$_3$)$_2$OSi(CH$_3$)$_3$]

75b [R = CF$_2$CF$_3$]
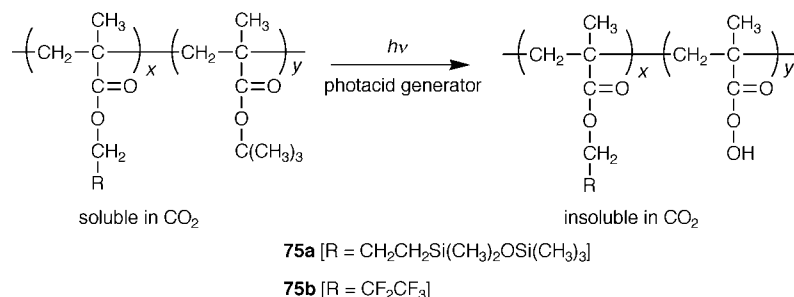
Scheme 4

using CO_2 flow rates of 25–40 g min^{-1} (190–440 bar, 70–120 °C). After extraction, the developed images were examined by microscopy (Fig. 21). The initial results were very promising, and excellent sensitivity and contrast were found for these novel lithographic materials. Although this process eliminates aqueous waste streams in the development step, it is still necessary to use organic solvents for the spin coating stage. As a rough indication of the scale of solvent usage, a processing line that produces 5000 finished silicon wafers per day will generate around 2000 gallons per day of waste organic solvent in addition to an equivalent amount of contaminated rinse water.[271] To address this issue, DeSimone[271] has studied the use of liquid CO_2 for spin coating, using CO_2-soluble polymeric resists of a broadly similar type to those used by Ober[270] and colleagues. The spin coating apparatus consists of a top-loading, medium-pressure vessel with a magnetic drive unit extending through the bottom of the chamber. The drive shaft is connected to a rotating chuck upon which the substrates are placed and rotated at speeds of up to 2500 rpm. The procedure used to cast a film is as follows. A silicon substrate is placed on the chuck, the vessel is sealed, and CO_2 is pumped into the vessel until the overall pressure is near the vapour pressure of liquid CO_2. The photoresist polymer is added in a separate view cell, where it is dissolved in liquid CO_2. The pressure in the main chamber is then increased to ≈ 0.3 bar below the vapour pressure of CO_2, to minimise evaporation effects during the spinning process. The polymer solution is then injected onto the centre of the substrate and the chuck is rotated. After venting the CO_2, a thin, solvent-free polymer film remains on the substrate (film thickness = 0.1–3 μm). The process obviously requires the use of liquid CO_2 as opposed to scCO$_2$, which limits the spin-coating temperature to less than 31.1 °C. This in turn dictates the solubility requirements for the resist materials and photoacid generators (*i.e.*, both materials must dissolve in liquid CO_2 at relatively low temperatures). Nevertheless, preliminary reports are extremely encouraging, suggesting that a process for microlithography may be possible where no organic solvents are used whatsoever, either in spin-coating procedure or in the development stage.

4 Summary

The use of carbon dioxide as a solvent presents a range of interesting opportunities in materials chemistry. In addition to reducing the need for toxic volatile organic solvents, CO_2 allows the synthesis of polymeric materials with well defined structures and properties. It is hoped that the chosen examples
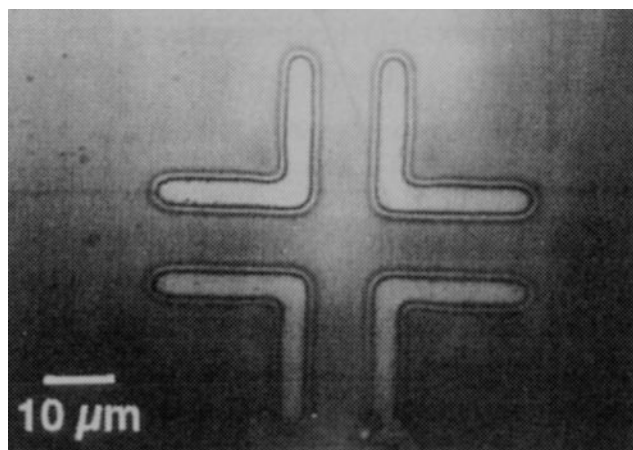
Fig. 21 Optical micrograph of an image on a silicon wafer generated by lithography using scCO$_2$ as the developing solvent (scale bar = 10 μm). Reproduced with permission from ref. 270, copyright Wiley-VCH.

have demonstrated that the advantages of using CO_2 might warrant the additional complexity associated with supercritical fluid technology, at least for some applications. Supercritical CO_2 is certainly not the answer to every materials chemistry problem, but one may speculate as to the general types of processes which stand to benefit most from the use of this solvent.

The anomalously high solubility of amorphous fluoropolymers makes the synthesis[11] and processing of these materials using CO_2 very attractive, particularly since the only other solvents tend to be fluorocarbons. In this respect the "solvent-free" application of fluorinated coatings from CO_2 is especially appealing.[269,271] The plasticisation of polymers by CO_2 plays a key role in the majority of the applications reviewed here. In a sense the addition of CO_2 to a polymer can be thought of as mimicking the effect of raising the temperature,[208b] and this may be very useful for the processing of thermally sensitive materials[265] or for low-temperature foaming processes *via* pressure quenching.[229–235] The addition of CO_2 has also been shown to reduce melt viscosity in bulk polycondensation reactions.[163–167] Due to its lack of toxicity, CO_2 is an ideal solvent for the preparation of materials where the elimination of toxic solvent residues is paramount. Thus, the formation of well defined polymer particles for applications such as controlled drug release is an important area of research. Similarly, there is potential for the use of scCO$_2$ for the impregnation of pharmaceutical molecules into preformed polymer particles. A promising approach here might be the use of the same techniques employed for disperse dyeing in scCO$_2$,[208–211] especially since many polar pharmaceuticals have low equilibrium solubilities in non-polar fluids.

The synthesis of polymers in CO_2 by heterogeneous polymerisation has potential to become a broad field in its own right, largely because of the development of novel stabilisers for dispersion polymerisation.[112] The main advantages arise from reductions in organic solvent usage and the ability to synthesise polymers with well defined particle morphologies that are comparable with polymers formed by conventional methods. Until now, the focus of this research has been batch processes, but there are many advantages to be gained from the development of continuous polymerisation processes using scCO$_2$. Continuous processes would allow reductions in reactor size, which is an important issue when considering the use of high pressure technology. Another important issue is the cost of the fluoropolymer and polysiloxane stabilisers used for dispersion polymerisation in CO_2. There are three possible approaches here: the development of less expensive alternatives, the optimisation of current materials such that they are effective at lower concentrations, or the introduction of methods to recover and recycle the stabiliser. In order to scale up these processes it would also be necessary to pay more attention to reactor design, since this is known to be an important factor in conventional dispersion polymerisation.[114]

There is growing evidence to show that compressed CO_2 is very useful for the synthesis of a range of well defined porous polymers.[152–161] The synthesis of these materials is traditionally solvent intensive, but the use of CO_2 can eliminate organic solvents altogether in some cases. The formation of polyurethane foams in CO_2 is a good example of an application which lies at the interface of polymer synthesis and processing.[152,153]

In summary, the application of carbon dioxide in polymer synthesis and processing has shown rapid development over the last ten years, and many of the fundamental principles underlying these techniques are now much more fully understood. It is anticipated that supercritical fluid technology will be used in the preparation of progressively more advanced materials in the future.

Acknowledgements

References

1 Reviews: (*a*) J. L. Kendall, D. A. Canelas, J. L. Young and J. M. DeSimone, *Chem. Rev.*, 1999, **99**, 543; (*b*) D. A. Canelas and J. M. DeSimone, *Adv. Polym. Sci.*, 1997, **133**, 103; (*c*) D. A. Canelas, A. L. C. Burke and J. M. DeSimone, *Plastics Eng.*, 1997, **53**, 37; (*d*) A. I. Cooper and J. M. DeSimone, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 761; (*e*) K. A. Shaffer and J. M. DeSimone, *Trends Polym. Sci.*, 1995, **3**, 146.

2 Reviews: (*a*) M. Aresta, *Quim. Nova*, 1999, **22**, 269; (*b*) B. Bungert, G. Sadowski and W. Arlt, *Ind. Eng. Chem. Res.*, 1998, **37**, 3208; (*c*) S. G. Kazarian, *Appl. Spectrosc. Rev.*, 1997, **32**, 301; (*d*) C. A. Eckert, B. L. Knutson and P. G. Debenedetti, *Nature (London)*, 1996, **383**, 313; (*e*) J. R. Lee and R. G. Kander, *ACS Symp. Ser.*, 1995, **603**, 131; (*f*) E. Kiran and J. F. Brennecke, *ACS Symp. Ser.*, 1993, **514**, 1; (*g*) Y. Garrabos, B. Leneindre, P. Subra, F. Cansell and C. Pommier, *Ann. Chim. Sci. Mater.*, 1992, **17**, 55.

3 M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction*, Butterworth-Heinemann, Stoneham, MA, 2nd edn., 1994.

4 P. G. Jessop and W. Leitner (Editors), *Chemical Synthesis using Supercritical Fluids*, Wiley-VCH, Weinheim, 1999; P. E. Savage, *Chem. Rev.*, 1999, **99**, 603.

5 A. Baiker, *Chem. Rev.*, 1999, **99**, 453; A. J. Mesiano, E. J. Beckman and A. J. Russell, *Chem. Rev.*, 1999, **99**, 623; M. G. Hitzler, F. R. Smail, S. K. Ross and M. Poliakoff, *Chem. Commun.*, 1998, 359; M. G. Hitzler and M. Poliakoff, *Chem. Commun.*, 1997, 1667.

6 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475; S. Kainz and W. Leitner, *Catal. Lett.*, 1998, **55**, 223.

7 (*a*) J. A. Darr and M. Poliakoff, *Chem. Rev.*, 1999, **99**, 495; (*b*) F. Cansell, B. Chevalier, A. Demourgues, J. Etourneau, C. Even, Y. Garrabos, V. Pessey, S. Petit, A. Tressaud and F. Weill, *J. Mater. Chem.*, 1999, **9**, 67.

8 O. Kajimoto, *Chem. Rev.*, 1999, **99**, 355.

9 S. C. Tucker, *Chem. Rev.*, 1999, **99**, 391.

10 J. A. Hyatt, *J. Org. Chem.*, 1984, **49**, 5097.

11 J. M. DeSimone, Z. Guan and C. S. Elsbernd, *Science*, 1992, **257**, 945.

12 C. F. Kirby and M. A. McHugh, *Chem. Rev.*, 1999, **99**, 565.

13 F. G. Keyes and J. G. Kirkwood, *Phys. Rev.*, 1930, **36**, 754.

14 R. C. Reid, J. M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 4th edn., 1987; W. Braker and A. L. Mossman, *Matheson Gas Data Book*, Matheson, Lyndhurst, NJ, 6th edn., 1980; K. J. Miller and J. A. Savchik, *J. Am. Chem. Soc.*, 1979, **101**, 7206.

15 Conversely, CO_2 is a feeble solvent for very polar polymers since dipole interactions outweigh quadrupole interactions, especially at low temperatures where polar interactions are magnified (see ref. 12).

16 (*a*) M. Lora, J. S. Lim and M. A. McHugh, *J. Phys. Chem. B*, 1999, **103**, 2818; (*b*) F. E. Hénon, M. Camaiti, A. L. C. Burke, R. G. Carbonell, J. M. DeSimone and F. Piacenti, *J. Supercrit. Fluids*, 1999, **15**, 173; (*c*) M. L. O'Neill, Q. Cao, M. Fang, K. P. Johnston, S. P. Wilkinson, C. D. Smith, J. L. Kerschner and S. H. Jureller, *Ind. Eng. Chem. Res.*, 1998, **37**, 3067; (*d*) G. Luna-Barcenas, S. Mawson, S. Takishima, J. M. DeSimone, I. C. Sanchez and K. P. Johnston, *Fluid Phase Equilib.*, 1998, **146**, 325; (*e*) C. A. Mertdogan, T. DiNoia and M. A. McHugh, *Macromolecules*, 1997, **30**, 7511; (*f*) C. Lepilleur, E. J. Beckman, H. Schinemann and V. J. Krukonis, *Fluid Phase Equilib.*, 1997, **134**, 285; (*g*) C. A. Mertdogan, H.-S. Byun, M. A. McHugh and W. H. Tuminello, *Macromolecules*, 1996, **29**, 6548; (*h*) P. Rindfleisch, T. P. DiNoia and M. A. McHugh, *J. Phys. Chem.*, 1996, **100**, 15581.

17 S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta and C. A. Eckert, *J. Am. Chem. Soc.*, 1996, **118**, 1729; S. G. Kazarian, M. F. Vincent and C. A. Eckert, *Rev. Sci. Instrum.*, 1996, **67**, 1586.

18 A. Dardin, J. B. Cain, J. M. DeSimone, C. S. Johnson and E. T. Samulski, *Macromolecules*, 1997, **30**, 3593; A. Dardin, J. M. DeSimone and E. T. Samulski, *J. Phys. Chem. B*, 1998, **102**, 1775.

19 J. F. Kadla, W. C. Bunyard and J. M. DeSimone, *Abstr. Pap. Am. Chem. Soc.*, 1999, **217**, 202.

20 A. I. Cooper, J. D. Londono, G. Wignall, J. B. McClain, E. T. Samulski, J. S. Lin, A. Dobrynin, M. Rubinstein, A. L. C. Burke, J. M. J. Fréchet and J. M. DeSimone, *Nature (London)*, 1997, **389**, 368.

21 M. D. Burford, M. Z. Ozel, A. A. Clifford, K. D. Bartle, Y. H. Lin, C. M. Wai and N. G. Smart, *Analyst (London)*, 1999, **124**, 609.

22 E. L. V. Goetheer, M. A. G. Vorstman and J. T. F. Keurentjes, *Chem. Eng. Sci.*, 1999, **54**, 1589; E. D. Niemeyer and F. V. Bright, *J. Phys. Chem. B*, 1998, **102**, 1474; M. P. Heitz, C. Carlier, J. deGrazia, K. L. Harrison, K. P. Johnston, T. W. Randolph and F. V. Bright, *J. Phys. Chem. B*, 1997, **101**, 6707; J. Eastoe, Z. Bayazit, S. Martel, D. C. Steytler and R. K. Heenan, *Langmuir*, 1996, **12**, 1423; K. A. Bartscherer, M. Minier and H. Renon, *Fluid Phase Equilib.*, 1995, **107**, 93.

23 G. B. Jacobson, C. T. Lee and K. P. Johnston, *J. Org. Chem.*, 1999, **64**, 1201; M. J. Clarke, K. L. Harrison, K. P. Johnston and S. M. Howdle, *J. Am. Chem. Soc.*, 1997, **119**, 6399.

24 M. Ji, X. Y. Chen, C. M. Wai and J. L. Fulton, *J. Am. Chem. Soc.*, 1999, **121**, 2631.

25 K. P. Johnston, K. L. Harrison, M. J. Clarke, S. M. Howdle, M. P. Heitz, F. V. Bright, C. Carlier and T. W. Randolph, *Science*, 1996, **271**, 624; M. R. Ehrhardt, P. F. Flynn and A. J. Wand, *J. Biomol. NMR*, 1999, **14**, 75.

26 The term "CO_2-philic" was first used by DeSimone and is now quite common in the literature. It refers to moieties which have an affinity for supercritical or liquid CO_2. Amorphous fluoropolymers and silicones tend to be CO_2-philic while polystyrene and poly(methyl methacrylate), for example, are both "CO_2-phobic" polymers.

27 J. S. Chiou, J. W. Barlow and D. R. Paul, *J. Appl. Polym. Sci.*, 1985, **30**, 2633.

28 M. Lee, C. B. Park and C. Tzoganakis, *Polym. Sci. Eng.*, 1999, **39**, 99.

29 Y. Zhang, K. K. Gangwani and R. M. Lemert, *J. Supercrit. Fluids*, 1997, **11**, 115.

30 R. G. Wissinger and M. E. Paulaitis, *Ind. Eng. Chem. Res.*, 1991, **30**, 842.

31 R. G. Wissinger and M. E. Paulaitis, *J. Polym. Sci., Part B: Polym. Phys.*, 1987, **25**, 2497.

32 W.-C. V. Wang, E. J. Kramer and W. H. Sachse, *J. Polym. Sci., Part B: Polym. Phys.*, 1982, **20**, 1371.

33 Y. T. Shieh, J. H. Su, G. Manivannan, P. H. C. Lee, S. P. Sawan and W. D. Spall, *J. Appl. Polym. Sci.*, 1996, **59**, 695.

34 T. Hirose, K. Mizoguchi and Y. Kamiya, *J. Polym. Sci., Part B: Polym. Phys.*, 1986, **24**, 2107.

35 Y. T. Shieh, J. H. Su, G. Manivannan, P. H. C. Lee, S. P. Sawan and W. D. Spall, *J. Appl. Polym. Sci.*, 1996, **59**, 707.

36 R. R. Edwards, Y. M. Tao, S. H. Xu, P. S. Wells, K. S. Yun and J. F. Parcher, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 2537.

37 Y. Kamiya, K. Mizoguchi, K. Terada, Y. Fujiwara and J.-S. Wang, *Macromolecules*, 1998, **31**, 472.

38 P. D. Condo and K. P. Johnston, *J. Polym. Sci., Part B: Polym. Phys.*, 1994, **32**, 523.

39 P. D. Condo, D. R. Paul and K. P. Johnston, *Macromolecules*, 1994, **27**, 365.

40 R. G. Wissinger and M. E. Paulaitis, *J. Polym. Sci., Part B: Polym. Phys.*, 1991, **29**, 631.

41 Y. Kamiya, K. Mizoguchi and Y. Naito, *J. Polym. Sci., Part B: Polym. Phys.*, 1990, **28**, 1955.

42 P. B. Smith and D. J. Moll, *Macromolecules*, 1990, **23**, 3250.

43 Y. Kamiya, K. Mizoguchi, T. Hirose and Y. Naito, *J. Polym. Sci., Part B: Polym. Phys.*, 1989, **27**, 879.

44 T. Banerjee and G. G. Lipscomb, *J. Appl. Polym. Sci.*, 1998, **68**, 1441.

45 B. J. Briscoe and C. T. Kelly, *Polymer*, 1995, **36**, 3099.

46 S. K. Goel and E. J. Beckman, *Polymer*, 1992, **33**, 5032.

47 S. K. Goel and E. J. Beckman, *Polymer*, 1993, **34**, 1410.

48 M. Lee, C. Tzoganakis and C. B. Park, *Polym. Sci. Eng.*, 1998, **38**, 1112.

49 S. Kato, T. Tsujita, H. Yoshimizu, T. Kinoshita and J. S. Higgins, *Polymer*, 1997, **38**, 2807.

50 A. Mokdad, A. Dubault and L. Monnerie, *J. Polym. Sci., Part B: Polym. Phys.*, 1996, **34**, 2723.

51 S. J. Barer and K. M. Stern, *ACS Symp. Ser.*, 1983, **363**, 1.

52 M. Hagiwara, H. Mitsui, S. Machi and T. Kagiya, *J. Polym. Sci., Part A*, 1968, **6**, 721.

53 P. Christian, S. M. Howdle, A. Gugel, I. Manners and J. Massey,

Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 1997, **214**, 246.

54 K. Ryu and S. Kim, *Kor. J. Chem. Eng.*, 1996, **13**, 415.

55 A. K. Chaudhary, E. J. Beckman and A. J. Russell, *J. Am. Chem. Soc.*, 1995, **117**, 3728.

56 M. S. Super and E. J. Beckmann, *Trends Polym. Sci.*, 1997, **5**, 236.

57 A.-F. Mingotaud and F. Cansell, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 343. (Note: Copies of these proceedings are available from I.S.A.S.F., ENSIC, 1 Rue Grandville – B. P. 451, F-54001 Nancy, France); A.-F. Mingotaud, F. Cansell, N. Gilbert and A. Soum, *Polym. J.*, 1999, **31**, 406.

58 K. M. Scholsky, *J. Supercrit. Fluids*, 1993, **6**, 103.

59 J. B. McClain, D. Londono, J. R. Combes, T. J. Romack, D. A. Canelas, D. E. Betts, G. D. Wignall, E. T. Samulski and J. M. DeSimone, *J. Am. Chem. Soc.*, 1996, **118**, 917.

60 The phase behaviour of PFOA in sub- and super-critical CO_2 has since been modelled with the statistical associated fluid theory (SAFT), see ref. 16(*d*).

61 Z. Guan, J. R. Combes, Y. Z. Menceloglu and J. M. DeSimone, *Macromolecules*, 1993, **26**, 2663.

62 A. M. van Herk, B. G. Manders, D. A. Canelas, M. A. Quadir and J. M. DeSimone, *Macromolecules*, 1997, **30**, 4780.

63 S. Beuermann, M. Buback, C. Isemer, C. Schmaltz and A. Wahl, *Proc. Int. Meeting GVC-Fachausschuß "High Pressure Chemical Engineering", Karlsruhe*, 1999, p. 17.

64 M. A. Quadir, J. M. DeSimone, A. M. vanHerk and A. L. German, *Macromolecules*, 1998, **31**, 6481.

65 S. Beuermann, M. Buback, C. Schmaltz and F. D. Kuchta, *Macromol. Chem. Phys.*, 1998, **199**, 1209.

66 S. Beuermann, M. Buback and C. Schmaltz, *Macromolecules*, 1998, **31**, 8069.

67 Z. Guan, C. S. Elsbernd and J. M. DeSimone, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1992, **34**, 329; M. Shaw, J. Ryan and C. Erkey, *Abstr. Pap. Am. Chem. Soc.*, 1997, **214**, 243; K. K. Kapellen, C. D. Mistele and J. M. DeSimone, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)*, 1996, **74**, 256; M. Poliakoff, S. M. Howdle and M. W. George, *Process Tech. Proc., 12: High Pressure Chemical Engineering*, eds. Ph. Rudolf von Rohr and CH. Trepp, Elsevier, Amsterdam, 1996, p. 67.

68 Z. Guan, J. R. Combes, C. S. Elsbernd and J. M. DeSimone, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1993, **34**, 329.

69 J. R. Combes, Z. Guan and J. M. DeSimone, *Macromolecules*, 1994, **27**, 865.

70 S. Beuermann, M. Buback, C. Isemer and A. Wahl, *Macromol. Rapid Commun.*, 1999, **20**, 26.

71 M. R. Clark and J. M. DeSimone, *Macromolecules*, 1995, **28**, 3002.

72 R. Arshady, *Colloid Polym. Sci.*, 1992, **270**, 717.

73 T. J. Romack, E. E. Maury and J. M. DeSimone, *Macromolecules*, 1995, **28**, 912.

74 Q. Xu, B. Han and H. Yan, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 337; H. Q. Hu, M. C. Chen, J. Li and G. M. Cong, *Acta Polym. Sinica*, 1998, 740; E. Dada, W. Lau, R. F. Merritt, Y. H. Paik and G. Swift, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Mater. Sci. Eng.)*, 1996, **74**, 427.

75 S. A. Mang, P. Dokolas and A. B. Holmes, *Org. Lett.*, 1999, **1**, 125.

76 T. J. Romack, J. M. DeSimone and T. A. Treat, *Macromolecules*, 1995, **28**, 8429.

77 T. J. Romack, B. E. Kipp and J. M. DeSimone, *Macromolecules*, 1995, **28**, 8432.

78 A. I. Cooper, W. P. Hems and A. B. Holmes, *Macromol. Rapid Commun.*, 1998, **19**, 353.

79 A. I. Cooper, W. P. Hems and A. B. Holmes, *Macromolecules*, 1999, **32**, 2156.

80 The copolymerisation of EDMA has also been investigated in near-critical and supercritical freon-22: J. R. Elliott and H. M. Cheung, *ACS Symp. Ser.*, 1993, **514**, 271.

81 T. Kagiya, M. Kondo, K. Narita and K. Fukui, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1688; R. H. Biddulph and P. H. Plesch, *J. Chem. Soc.*, **1960**, 3913; T. Pernecker and J. P. Kennedy, *Polym. Bull. (Berlin)*, 1994, **32**, 537; **33**, 13; J. P. Kennedy, *Trends Polym. Sci.*, 1995, **3**, 386.

82 See for example: J. M. G. Cowie, *Polymer Chemistry & Physics of Modern Materials*, Blackie A & P, London, 2nd edn., 1991, ch. 4.

83 T. Higashimura and M. Sawamoto, *Makromol. Chem., Macro-mol. Chem. Phys.*, **1985**, 153; T. D. Shaffer, *ACS Symp. Ser.*, 1997, **665**, 1.

84 While this may be true, as Kendall *et al.*[1a] point out many cationic polymerisations are performed at low temperatures (-70 to $-30\,^\circ C$) where CO_2 would exist in the liquid state. Under liquid conditions, the compressibility of the solvent would be very much lower.

85 M. R. Clark, J. L. Kendall and J. M. DeSimone, *Macromolecules*, 1997, **30**, 6011.

86 R. E. Farncomb and G. W. Nauflett, *Waste Management*, 1997, **17**, 123.

87 C. D. Mistele, H. H. Thorp and J. M. DeSimone, *J. Macromol. Sci., Pure Appl. Chem.*, 1996, **A33**, 953.

88 J. G. Hamilton, J. J. Rooney, J. M. DeSimone and C. Mistele, *Macromolecules*, 1998, **31**, 4387.

89 S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, **115**, 9858; P. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2039; P. Schwab, R. H. Grubbs and J. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100.

90 R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare and M. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875.

91 A. Fürstner, D. Koch, K. Langemann, W. Leitner and C. Six, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2466.

92 H. Hori, C. Six and W. Leitner, *Macromolecules*, 1999, **32**, 3178.

93 (*a*) T. J. de Vries, M. A. G. Vorstman and J. T. F. Keurentjes, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 71; (*b*) T. J. de Vries, M. A. G. Vorstman and J. T. F. Keurentjes, *Proc. Int. Meeting GVC-Fachausschuß "High Pressure Chemical Engineering", Karlsruhe*, 1999, p. 21

94 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414; S. Mecking, L. K. Johnson, L. Wang and M. Brookhart, *J. Am. Chem. Soc.*, 1998, **120**, 888.

95 However, it is difficult to compare these results because the reaction conditions were not exactly equivalent in the two sets of experiments.

96 B. Folie and M. Radosz, *Ind. Eng. Chem. Res.*, 1995, **34**, 1501; T. E. Bitterwolf, J. T. Bays, S. Gallagher, J. C. Linehan and C. R. Yonker, *Abstr. Pap. Am. Chem. Soc.*, 1997, **213**, 6.

97 (*a*) S. J. Chen and M. Radosz, *Macromolecules*, 1992, **25**, 3089; (*b*) B. Folie, M. Kelchtermans, J. R. Shutt, H. Schonemann and V. Krukonis, *J. Appl. Polym. Sci.*, 1997, **64**, 2015.

98 D. J. Darensbourg, N. W. Stafford and T. Katsurao, *J. Mol. Catal. A, Chem.*, 1995, **104**, L1.

99 D. J. Darensbourg and M. W. Holtcamp, *Macromolecules*, 1995, **28**, 7577.

100 D. J. Darensbourg and M. W. Holtcamp, *Coord. Chem. Rev.*, 1996, **153**, 155.

101 M. Super, E. Berluche, C. Costello and E. Beckman, *Macromolecules*, 1997, **30**, 368.

102 M. Super and E. J. Beckman, *Macromol. Symp.*, 1998, **127**, 89.

103 M. Super, R. M. Enick and E. J. Beckman, *J. Chem. Eng. Data*, 1997, **42**, 664.

104 S. A. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 323.

105 This chromium complex is very similar to the iron porphyrin catalyst used by Tumas for selective aerobic oxidations in $scCO_2$: E. R. Birnbaum, R. M. LeLacheur, A. C. Horton and W. Tumas, *J. Mol. Catal. A, Chem.*, 1999, **139**, 11.

106 S. A. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Macromolecules*, in press.

107 S. Asano, T. Aida and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1985, 1148.

108 M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1998, **120**, 11018.

109 K. K. Kappellen, C. D. Mistele and J. M. DeSimone, *Macromolecules*, 1996, **29**, 495.

110 F. M. Kerton, G. A. Lawless and S. P. Armes, *J. Mater. Chem.*, 1997, **7**, 1965.

111 Y. Fu, D. R. Palo, C. Erkey and R. A. Weiss, *Macromolecules*, 1997, **30**, 7611.

112 J. M. DeSimone, E. E. Maury, Y. Z. Menceloglu, J. B. McClain, T. J. Romack and J. R. Combes, *Science*, 1994, **265**, 356.

113 D. C. Blackley, *Emulsion Polymerization*, Wiley, New York, 1975; R. G. Gilbert, *Emulsion Polymerization: A Mechanistic Approach*, Academic Press, London, 1995.

114 K. E. J. Barrett, *Dispersion Polymerization in Organic Media*, Wiley, London, 1975.

115 In any case, many of the solvents commonly used for dispersion polymerisation have dielectric constants which are too low for electrostatic stabilisation to play a significant role. This would certainly apply to CO_2 (dielectric constant = 1.01–1.67, see ref. 13).
116 K. A. Consani and R. D. Smith, *J. Supercrit. Fluids*, 1990, **3**, 51.
117 Y.-L. Hsiao, E. E. Maury, J. M. DeSimone, S. Mawson and K. P. Johnston, *Macromolecules*, 1995, **28**, 8159.
118 Y.-L. Hsiao and J. M. DeSimone, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 2009.
119 D. A. Canelas, D. E. Betts, J. M. DeSimone, M. Z. Yates and K. P. Johnston, *Macromolecules*, 1998, **31**, 6794.
120 H. Shiho and J. M. DeSimone, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 2429.
121 D. Wang and J. M. DeSimone, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)*, 1999, **80**, 526.
122 A helium "head pressure" is often used in CO_2 cylinders used for applications such as supercritical fluid extraction and super-critical fluid chromatography. Helium has low but finite miscibility with liquid CO_2, which can apparently have a significant effect on the solvent character (see for example: J. W. King, J. H. Johnson and F. J. Eller, *Anal. Chem.*, 1995, **67**, 2288).
123 (*a*) G. D. Wignall, *J. Phys., Condens. Matter*, 1999, **11**, 157; (*b*) S. Q. Zhou and B. Chu, *Macromolecules*, 1998, **31**, 5300; (*c*) D. Chillura-Martino, R. Triolo, J. B. McClain, J. R. Combes, D. E. Betts, D. A. Canelas, J. M. DeSimone, E. T. Samulski, H. D. Cochran, J. D. Londono and G. Wignall, *J. Mol. Struct.*, 1996, **383**, 3; (*d*) J. L. Fulton, D. M. Pfund, J. B. McClain, T. R. Romack, E. E. Maury, J. R. Combes, E. T. Samulski, J. M. DeSimone and M. Capel, *Langmuir*, 1995, **11**, 4241.
124 K. A. Shaffer, T. A. Jones, D. A. Canelas and J. M. DeSimone, *Macromolecules*, 1996, **29**, 2704.
125 M. L. O'Neill, M. Z. Yates, K. P. Johnston, C. D. Smith and S. P. Wilkinson, *Macromolecules*, 1998, **31**, 2838.
126 M. L. O'Neill, M. Z. Yates, K. P. Johnston, C. D. Smith and S. P. Wilkinson, *Macromolecules*, 1998, **31**, 2848.
127 J. N. Hay, R. J. Winder, M. R. Giles and S. M. Howdle, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 121.
128 P. Christian, M. R. Giles, S. M. Howdle, R. C. Major and J. N. Hay, *Polymer*, 2000, **41**, 1251.
129 It is also worth noting that Christian *et al.* used an overhead blade stirrer, while Shaffer *et al.* used a magnetic stir bar to mix their reactions. Presumably, the overhead stirrer gave rise to more vigorous agitation.
130 C. Lepilleur and E. J. Beckman, *Macromolecules*, 1997, **30**, 745.
131 E. E. Maury, H. J. Batten, S. K. Killian, Y. Z. Menceloglu, J. R. Combes and J. M. DeSimone, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1993, **34**, 664.
132 D. A. Canelas and J. M. DeSimone, *Macromolecules*, 1997, **30**, 5673.
133 K. L. Harrison, S. R. P. daRocha, M. Z. Yates, K. P. Johnston, D. A. Canelas and J. M. DeSimone, *Langmuir*, 1998, **14**, 6855.
134 K. L. Harrison, K. P. Johnston and I. C. Sanchez, *Langmuir*, 1996, **12**, 2637.
135 D. A. Canelas, D. E. Betts and J. M. DeSimone, *Macromolecules*, 1996, **29**, 2818.
136 T.-M. Yong, W. P. Hems, J. L. M. van Nunen, A. B. Holmes, J. H. G. Steinke, P. L. Taylor, J. A. Segal and D. A. Griffin, *Chem. Commun.*, 1997, 1811.
137 W. P. Hems, T.-M. Yong, J. L. M. van Nunen, A. I. Cooper, A. B. Holmes and D. A. Griffin, *J. Mater. Chem.*, 1999, **9**, 1403.
138 A. I. Cooper, W. P. Hems and A. B. Holmes, 1999, in preparation.
139 K. T. Lim, S. E. Webber and K. P. Johnston, *Macromolecules*, 1999, **32**, 2811.
140 M. Z. Yates, G. Li, J. J. Shim, S. Maniar, K. P. Johnston, K. T. Lim and S. Webber, *Macromolecules*, 1999, **32**, 1108.
141 F. Rindfleisch, R. Becker and W. D. Hergeth, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)*, 1999, **80**, 518.
142 The authors observed that the PDMS block in PS-b-PDMS stabilisers was decomposed by the $TiCl_4$ catalyst.
143 J. C. Meredith and K. P. Johnston, *Macromolecules*, 1998, **31**, 5507; 5518; D. G. Peck and K. P. Johnston, *J. Phys. Chem.*, 1993, **97**, 5661; *Macromolecules*, 1993, **26**, 1537.
144 M. L. O'Neill, M. Z. Yates, K. P. Johnston, K. L. Harrison, K. P. Johnston, D. A. Canelas, D. E. Betts, J. M. DeSimone and S. P. Wilkinson, *Macromolecules*, 1997, **30**, 5050.
145 M. Z. Yates, M. L. O'Neill, K. P. Johnston, S. Webber,

D. A. Canelas, D. E. Betts and J. M. DeSimone, *Macromolecules*, 1997, **30**, 5060.
146 H. G. Yuan, G. Kalfas and W. H. Ray, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, 1991, **C31**, 215; E. Vivaldo-Lima, P. E. Wood, A. E. Hamielec and A. Penlidis, *Ind. Eng. Chem. Res.*, 1997, **36**, 939.
147 F. A. Adamsky and E. J. Beckman, *Macromolecules*, 1994, **27**, 312 (see also correction in *Macromolecules*, 1994, **27**, 5238).
148 The inverse emulsion polymerisation of acrylamide has also been carried out in near-critical and supercritical ethane/propane: E. J. Beckman, J. L. Fulton, D. W. Matson and R. D. Smith, *ACS Symp. Ser.*, 1989, **406**, 184.
149 D.-W. Zhu, *Macromolecules*, 1996, **29**, 2813; A. G. Mayes and K. Mosbach, *Anal. Chem.*, 1996, **68**, 3769; R. J. Ansell and K. Mosbach, *J. Chromatogr. A*, 1997, **787**, 55.
150 M. A. Quadir, R. Snook, R. G. Gilbert and J. M. DeSimone, *Macromolecules*, 1997, **30**, 6015.
151 D. C. Sherrington, *Chem. Commun.*, 1998, 2275; *Macromol. Chem., Macromol. Symp.*, 1993, **70/71**, 303
152 K. L. Parks and E. J. Beckman, *Polym. Eng. Sci.*, 1996, 36 (a) 2404; (b) 2417.
153 R. Enick, E. Beckman, C. M. Shi and E. Karmana, *J. Supercrit. Fluids*, 1998, **13**, 127.
154 F. Svec and J. M. J. Fréchet, *Ind. Eng. Chem. Res.*, 1998, **38**, 34; *Science*, 1996, **273**, 205.
155 A. I. Cooper and A. B. Holmes, *Adv. Mater.*, 1999, **11**, 1270.
156 X. X. Zhu, K. Banana and R. Yen, *Macromolecules*, 1997, **30**, 3031.
157 X. X. Zhu, K. Banana, H. Y. Liu, M. Krause and M. Yang, *Macromolecules*, 1999, **32**, 277.
158 D. A. Loy, E. M. Russick, S. A. Yamanaka, B. M. Baugher and K. J. Shea, *Chem. Mater.*, 1997, **9**, 2264.
159 H. Dislich, *J. Non-Cryst. Solids*, 1986, **80**, 115; H. Schmidt, *J. Non-Cryst. Solids*, 1988, **100**, 51; C. J. Brinker and G. W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, 1990; D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431.
160 J. Fricke, *Springer Proc. Phys.*, 1986, **6**, 2; L. W. Hrubesh, *Chem. Ind.*, 1990, 824.
161 K. G. Sharp, *J. Sol–Gel Sci. Technol.*, 1994, **2**, 35.
162 A. L. C. Burke, R. D. Givens, M. Jikei and J. M. DeSimone, *Polym. Prepr.*, 1997, **38**, 387; R. D. Givens, M. Jikei and J. M. DeSimone, *Polym. Prepr.*, 1997, **38**, 468.
163 P. G. Odell and G. K. Hamer, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1997, **38**, 470.
164 In fact, at the high temperatures often used for melt phase polycondensation, the CO_2 density need not necessarily be very high in order to "flush out" the condensate, which tends to be in the vapour state in any case.
165 S. M. Gross, D. Flowers, G. Roberts, D. J. Kiserow and J. M. DeSimone, *Macromolecules*, 1999, **32**, 3167 (see also correction in *Macromolecules*, 1999, **32**, 3170).
166 A. L. C. Burke, G. Maier and J. M. DeSimone, *Abstr. Pap. Am. Chem. Soc.*, 1996, **211**, 152.
167 R. D. Givens, M. Jikei and J. M. DeSimone, *Polym. Prepr.*, 1997, **38**, 468.
168 Presumably polymerisation in the surrounding CO_2 phase may be a problem under these conditions, unless some method is used to inhibit solution polymerisation (see for example: J. Jagur-Grodzinski, *Heterogeneous Modification of Polymers, Matrix and Surface Reactions*, Wiley, Chichester, UK, 1997).
169 J. J. Watkins and T. J. McCarthy, *Macromolecules*, 1994, **27**, 4845.
170 J. J. Watkins and T. J. McCarthy, *Macromolecules*, 1995, **28**, 4067.
171 E. Kung, A. J. Lesser and T. J. McCarthy, *Macromolecules*, 1997, **31**, 4160.
172 O. Muth, T. Hirth and H. Vogel, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 127.
173 K. A. Arora, A. J. Lesser and T. J. McCarthy, *Macromolecules*, 1999, **32**, 2562.
174 P. Rajagopalan and T. J. McCarthy, *Macromolecules*, 1998, **31**, 4791.
175 See for example ref. 3, ch. 9, pp. 192–292.
176 L. J. D. Britto, J. B. P. Soares, A. Penlidis and V. Krukonis, *J. Polym. Sci., Part B: Polym. Phys.*, 1999, **37**, 553; J. A. Pratt and M. A. McHugh, *J. Supercrit. Fluids*, 1996, **9**, 61.
177 I. Yilgör and J. E. McGrath, *Polym. Bull.*, 1984, **12**, 491; I. Yilgör, J. E. McGrath and V. J. Krukonis, *Polym. Bull.*, 1984, **12**, 499.

178 S. Kim, Y. S. Kim and S. B. Lee, *J. Supercrit. Fluids*, 1998, **13**, 99; S. Rey and F. Cansell, *Polym. J.*, 1998, **30**, 863; F. Cansell, P. Botella, J. L. Six, Y. Garrabos, R. Tufeu and Y. Gnanou, *Polym. J.*, 1997, **29**, 910.

179 A. A. Clifford, K. D. Bartle, I. Gelebart and S. Zhu, (a) *Polymer*, 1998, **39**, 6037; (b) *J. Chromatogr. A*, 1997, **785**, 395.

180 K. Robards, P. R. Haddad and P. E. Jackson, *Principles and Practice of Modern Chromatographic Methods*, Academic Press, London, 1994.

181 T. L. Chester, J. D. Pinkston and D. E. Raynie, *Anal. Chem.*, 1998, **70**, 301; J. A. Blackwell, R. W. Stringham and J. D. Weckwerth, *Anal. Chem.*, 1997, **69**, 409; T. L. Chester, J. D. Pinkston and D. E. Raynie, *Anal. Chem.*, 1996, **68**, 487.

182 H. Pasch, *Adv. Polym. Sci.*, 1997, **128**, 1.

183 K. Maeda and Y. Okamoto, *Kobun. Ronbun.*, 1997, **54**, 608.

184 K. Hatada, T. Nishiura, T. Kitayama and K. Ute, *Macromol. Symp.*, 1997, **118**, 135.

185 K. Hatada, *Trends Polym. Sci.*, 1997, **5**, 223.

186 K. Ute, Y. Yamasaki, M. Naito, N. Miyatake and K. Hatada, *Polym. J.*, 1995, **27**, 951.

187 K. Ute, N. Miyatake, Y. Osugi and K. Hatada, *Polym. J.*, 1993, **25**, 1153.

188 N. J. Wu, Y. F. Shen, V. Lopez-Avila and M. L. Lee, *J. Microcolumn Sep.*, 1999, **11**, 287.

189 R. Enick, E. Beckman, A. Yazdi, V. Krukonis, H. Schonemann and J. Howell, *J. Supercrit. Fluids*, 1998, **13**, 121.

190 M. Perut and V. Perut, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 141.

191 C. A. Mertdogan, M. A. McHugh, H. G. Barth, D. J. Walls and W. H. Tuminello, *Int. J. Polym. Anal. Char.*, 1998, **4**, 231.

192 B. Bungert, G. Sadowski and W. Arlt, *Fluid Phase Equilib.*, 1997, **139**, 349.

193 M. A. Winters, D. Z. Frankel, P. G. Debenedetti, J. Carey, M. Devaney and T. M. Przybycien, *Biotechnol. Bioeng.*, 1999, **62**, 247.

194 S. D. Yeo, G. B. Lim, P. G. Debenedetti and H. Bernstein, *Biotechnol. Bioeng.*, 1993, **41**, 341; M. A. Winters, B. L. Knutson, P. G. Debenetti, H. G. Sparks, T. M. Przybycien, C. L. Stevenson and S. J. Prestrelski, *J. Pharm. Sci.*, 1996, **85**, 586.

195 L. T. Taylor, *Supercritical Fluid Extraction*, Wiley, New York, 1996.

196 H. J. Vandenburg, A. A. Clifford, K. D. Bartle, J. Carroll, I. Newton, L. M. Garden, J. R. Dean and C. T. Costley, *Analyst (London)*, 1997, **122**, R101.

197 K. D. Bartle, A. A. Clifford, S. B. Hawthorne, J. J. Lagenfield, D. J. Miller and R. Robinson, *J. Supercrit. Fluids*, 1990, **3**, 143; K. D. Bartle, T. Boddington, A. A. Clifford, N. J. Cotton and C. J. Dowle, *Anal. Chem.*, 1991, **63**, 143; K. D. Bartle, T. Boddington, A. A. Clifford and S. B. Hawthorne, *J. Supercrit. Fluids*, 1992, **5**, 207; A. A. Clifford, K. D. Bartle and S. A. Zhu, *Anal. Proc.*, 1995, **32**, 227.

198 (a) K. M. Dooley, D. Launey, J. M. Becnel and T. L. Caines, *ACS Symp. Ser.*, 1995, **608**, 269; (b) X. Lou, H.-G. Janssen and C. A. Cramers, *J. Microcolumn. Sep.*, 1995, **7**, 303.

199 See ref. 196 and refs. therein.

200 A. M. Pinto and L. T. Taylor, *J. Chromatogr. A*, 1998, **811**, 163.

201 J. Chunyue, P. Qinmin and P. Zuren, *Chin. J. Chem. Eng.*, 1998, **6**, 239.

202 A. Venema, H. J. F. M. Vandeven, F. David and P. Sandra, *J. High Resolut. Chromatogr.*, 1993, **16**, 522.

203 N. J. Cotton, K. D. Bartle, A. A. Clifford, S. Ashraf, R. Moulder and C. J. Dowle, *J. High Resolut. Chromatogr.*, 1991, **14**, 164.

204 G. Filardo, A. Galia, S. Gambino, G. Silvestri and M. Poidomani, *J. Supercrit. Fluids*, 1996, **9**, 234.

205 R. E. Zacharia, S. L. Simon, E. J. Beckman and R. M. Enick, *Polym. Degrad. Stab.*, 1999, **63**, 85.

206 E. Sahl-Demessie, K. L. Levien and J. J. Morrell, *Chemtech.*, 1998, **28**, 12.

207 The impregnation of porous supports using scCO$_2$ may also prove useful for the preparation of controlled drug delivery systems: C. Domingo, J. García-Carmona, J. Llibre and R. Rodríguez-Clemente, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 101.

208 (a) S. G. Kazarian, N. H. Brantley and C. A. Eckert, *Chemtech.*, 1999, **29**, 36; (b) S. G. Kazarian, B. J. Briscoe and C. J. Lawrence *Polymer Process Engineering 99*, ed. P. D. Coates, Institute of Materials, London, 1999, p. 28.

209 B. L. West, S. G. Kazarian, M. F. Vincent, N. H. Brantley and C. A. Eckert, *J. Appl. Polym. Sci.*, 1998, **69**, 911.

210 S. G. Kazarian, N. H. Brantley, B. L. West, M. F. Vincent and C. A. Eckert, *Appl. Spectrosc.*, 1997, **51**, 491.

211 S. G. Kazarian, M. F. Vincent, B. L. West and C. A. Eckert, *J. Supercrit. Fluids*, 1998, **13**, 107; S. G. Kazarian, B. L. West, M. F. Vincent and C. A. Eckert, *Am. Lab.*, 1997, **29**, B18.

212 D. Knittel, W. Saus, S. Hoger and E. Schollmeyer, *Angew. Makromol. Chem.*, 1994, **218**, 69.

213 P. L. Beltrame, A. Castelli, E. Selli, L. Villani, A. Mossa, A. Seves and G. Testa, *Dyes Pigments*, 1998, **39**, 35.

214 X. Ma and D. L. Tomasko, *Ind. Eng. Chem. Res.*, 1997, **36**, 1586.

215 S. E. Barry and D. S. Soane, *Macromolecules*, 1996, **29**, 3565.

216 S. M. Howdle, J. M. Ramsay and A. I. Cooper, *J. Polym. Sci., Part B: Polym. Phys.*, 1994, **32**, 541.

217 A. I. Cooper, S. M. Howdle, C. Hughes, M. Jobling, S. G. Kazarian, M. Poliakoff, L. Shepherd and K. P. Johnston, *Analyst (London)*, 1993, **118**, 1111.

218 S. G. Kazarian, S. M. Howdle and M. Poliakoff, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1275; A. I. Cooper, S. G. Kazarian and M. Poliakoff, *Chem. Phys. Lett.*, 1993, **206**, 175.

219 V. K. Popov, V. N. Bagratashvili, A. P. Krasnov, E. E. SaidGaliyev, L. N. Nikitin, O. V. Afonicheva and A. D. Aliev, *Tribol. Lett.*, 1998, **5**, 297.

220 J. J. Watkins and T. J. McCarthy, *Chem. Mater.*, 1995, **7**, 1991.

221 M. Yalpani, *Polymer*, 1993, **34**, 1102.

222 H. J. Hayes and T. J. McCarthy, *Macromolecules*, 1998, **31**, 4813.

223 J. M. de Gooijer and C. E. Koning, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 205.

224 C. Dispenza, G. Filardo, G. Silvestri and G. Spadaro, *Colloid. Polym. Sci.*, 1997, **275**, 390; G. Filardo, S. Gambino, G. Silvestri, E. Calderaro and G. Spadaro, *Radiat. Phys. Chem.*, 1994, **44**, 597.

225 G. Filardo, C. Dispenza, G. Silvestri and G. Spadaro, *J. Supercrit. Fluids*, 1998, **12**, 177.

226 G. Spadaro, G. Filardo, R. De Gregorio, A. Galia, A. Valenza, C. Koning and M. van Duin, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 221.

227 T. Yarita, T. Ihara, Y. Horimoto and A. Nomura, *Anal. Sci.*, 1999, **15**, 377.

228 A. T. Young, Jr., *Cell. Plastics*, 1987, 23rd Jan., p. 55.

229 S. K. Goel and E. J. Beckman, *Cell. Polym.*, 1993, **12**, 251.

230 S. K. Goel and E. J. Beckman, *Polym. Eng. Sci.*, 1994, **34**, 1137; 1148

231 S. K. Goel and E. J. Beckman, *AIChE J.*, 1995, **41**, 357.

232 K. A. Arora, A. J. Lesser and T. J. McCarthy, *Macromolecules*, 1998, **31**, 4614.

233 K. A. Arora, A. J. Lesser and T. J. McCarthy, *Polym. Eng. Sci.*, 1998, **38**, 2055.

234 M.-T. Liang and C.-M. Wang, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 151.

235 K. N. Lee, Y. J. Suh, H. J. Lee and J. H. Kim, *Polymer (Korea)*, 1999, **23**, 181.

236 See for example: B. Subramaniam, R. A. Rajewski and K. Snavely, *J. Pharm. Sci.*, 1997, **86**, 885; B. Y. Shekunov, M. Hanna and P. York, *J. Cryst. Growth*, 1999, **199**, 1345; R. E. Sievers, U. Karst, P. D. Milewski, S. P. Sellers, B. A. Miles, J. D. Schaefer, C. R. Stoldt and C. Y. Wu, *Aerosol Sci. Technol.*, 1999, **30**, 3.

237 E. Reverchon, G. Della Porta, A. Di Triolio and S. Pace, *Ind. Eng. Chem. Res.*, 1998, **37**, 952.

238 J. A. Banister, P. D. Lee and M. Poliakoff, *Organometallics*, 1995, **14**, 3876; J. R. Williams, A. A. Clifford, K. D. Bartle and T. P. Kee, *Powder Technol.*, 1998, **96**, 158.

239 For example, supercritical solvents such as pentane and CHClF$_2$ have been used for the formation of polymer particles and fibres by RESS: (a) R. C. Petersen, D. W. Matson and R. D. Smith, *Polym. Eng. Sci.*, 1987, **27**, 1693; (b) A. K. Lele and A. D. Shine, *AIChE J.*, 1992, **38**, 742.

240 E. Reverchon, *J. Supercrit. Fluids*, 1999, **15**, 1.

241 P. Subra and P. Jestin, *Powder Technol.*, 1999, **103**, 2.

242 J. W. Tom and P. G. Debenedetti, *J. Aerosol Sci.*, 1991, **22**, 555; P. G. Debenedetti, J. W. Tom, X. Kwauk and S.-D. Yeo, *Fluid Phase Equilib.*, 1993, **82**, 311.

243 S. Mawson, K. P. Johnston, J. R. Combes and J. M. Desimone, *Macromolecules*, 1995, **28**, 3182.

244 J. W. Tom and P. G. Debenedetti, *Biotechnol. Prog.*, 1991, **7**, 403.

245 L. Benedetti, A. Bertucco and P. Pallado, *Biotechnol. Bioeng.*, 1997, **53**, 232.

246 K. Mishima, K. Matsuyama, Y. Taruta, M. Ezawa, Y. Ito and M. Nagatani, *Stud. Surf. Sci. Catal.*, 1998, **114**, 661.

247 J. W. Tom, G. B. Lim, P. G. Debenedetti and R. K. Prud'homme, *ACS Symp. Ser.*, 1993, **514**, 238; P. G. Debenedetti, J. W. Tom, S. D. Yeo and G. B. Lim, *J. Controlled Release*, 1993, **24**, 27.

248 J. W. Tom, P. G. Debenedetti and R. Jerome, *J. Supercrit. Fluids*, 1994, **7**, 9.
249 J.-H. Kim, T. E. Paxton and D. L. Tomasko, *Biotechnol. Prog.*, 1996, **12**, 650.
250 J. Bleich and B. W. Muller, *J. Microencapsulation*, 1996, **13**, 131.
251 J. Bleich, P. Kleinebudde and B. W. Müller, *Int. J. Pharm.*, 1994, **106**, 77.
252 J. Thies and B. W. Muller, *Eur. J. Pharm. Biopharm.*, 1998, **45**, 67.
253 R. Falk, T. W. Randolph, J. D. Meyer, R. M. Kelly and M. C. Manning, *J. Controlled Release*, 1997, **44**, 77.
254 R. F. Falk and T. W. Randolph, *Pharm. Res.*, 1998, **15**, 1233.
255 T. J. Young, K. P. Johnston, K. Mishima and H. Tanaka, *J. Pharm. Sci.*, 1999, **88**, 640.
256 R. Ghaderi, P. Artursson and J. Carlfors, *Pharm. Res.*, 1999, **16**, 676.
257 R. Sloan, M. Tservistas, M. E. Hollowood, L. Sarup, G. O. Humphreys, P. York, W. Ashraf and M. Hoare, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 169.
258 S. D. Yeo, P. G. Debenedetti, M. Radosz and H. W. Schmidt, *Macromolecules*, 1993, **26**, 6207.
259 S. D. Yeo, P. G. Debenedetti, M. Radosz, R. Giesa and H. W. Schmidt, *Macromolecules*, 1995, **28**, 1316.
260 K. J. Heater and D. L. Tomasko, *J. Supercrit. Fluids*, 1998, **14**, 55.
261 D. J. Dixon, K. P. Johnston and R. A. Bodmeier, *AIChE J.*, 1993, **39**, 127.
262 D. J. Dixon, G. Luna-Bárcenas and K. P. Johnston, *Polymer*, 1994, **35**, 3998.
263 S. Mawson, S. Kanakia and K. P. Johnston, *J. Appl. Polym. Sci.*, 1997, **64**, 2105.
264 (*a*) S. Mawson, K. P. Johnston, D. E. Betts, J. B. McClain and J. M. DeSimone, *Macromolecules*, 1997, **30**, 71; (*b*) S. Mawson, M. Z. Yates, M. L. O'Neill and K. P. Johnston, *Langmuir*, 1997, **13**, 1519.
265 S. M. Howdle, F. S. Mandel, J. D. Wang, V. K. Popov, K. M. Shakesheff and M. C. Davies, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 15; F. S. Mandel, *Proc. 5th Meeting on Supercritical Fluids, Chemistry and Materials, Nice*, 1998, T1, 69
266 E. Weidner, M. Petermann, K. Blatter and H. U. Simmrock, *Proc. 6th Meeting on Supercritical Fluids, Chemistry and Materials, Nottingham*, 1999, p. 95; E. Weidner, *Proc. Int. Meeting GVC-Fachausschuß "High Pressure Chemical Engineering", Karlsruhe*, 1999, p. 217.
267 D. C. Busby, C. W. Glancy, K. L. Hoy, A. C. Kuo, C. Lee and K. A. Nielsen, *Surf. Coat. Int.*, 1991, **74**, 362.
268 M. D. Donohue, J. L. Geiger, A. A. Kiamos and K. A. Nielsen, *ACS Symp. Ser.*, 1996, **626**, 152.
269 F. E. Henon, M. Camaiti, A. L. C. Burke, R. G. Carbonell, J. M. DeSimone and F. Piacenti, *J. Supercrit. Fluids*, 1999, **15**, 173.
270 C. K. Ober, A. H. Gabor, P. GallagherWetmore and R. D. Allen, *Adv. Mater.*, 1997, **9**, 1039.
271 J. M. DeSimone, *Proc. Polymer '98 Meeting, "The New Polymers", Science, Technology & Applications, Brighton*, 1998, p.5.

Paper a906486i