1
Supercritical Carbon Dioxide for Sustainable Polymer Processes *

Maartje Kemmere

1.1
Introduction

Environmental and human safety concerns have become determining factors in chemical engineering and process development. Currently, there is a strong emphasis on the development of more sustainable processes, particularly in the polymer industry. Many conventional production routes involve an excessive use of organic solvents, either as a reaction medium in the polymerization step or as a processing medium for shaping, extraction, impregnation, or viscosity reduction. In each of these steps, most of the effort of the process is put into the solvent recovery, as schematically indicated in Fig. 1.1 for the polymerization step.

Illustrative examples include the production of butadiene rubber, with a product/solvent ratio of 1:6 [1], and the production of elastomers such as EPDM (ethylene-propylene-diene copolymer) in an excess of hexane [2]. Annually, these types of processes add substantially to the total emissions of volatile organic
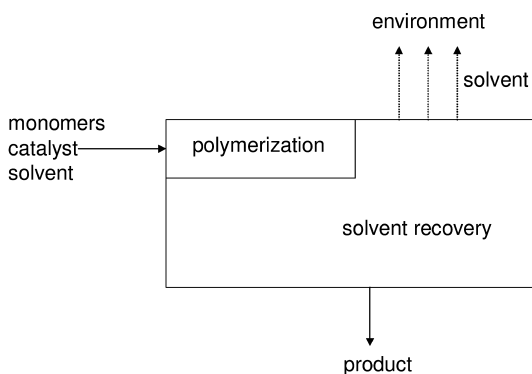

Fig. 1.1 Visualization of the relative effort required for polymerization and solvent recovery in conventional catalytic polymerization processes based on organic solvents.

* The symbols used in this chapter are listed at the end of the text, under "Notation".
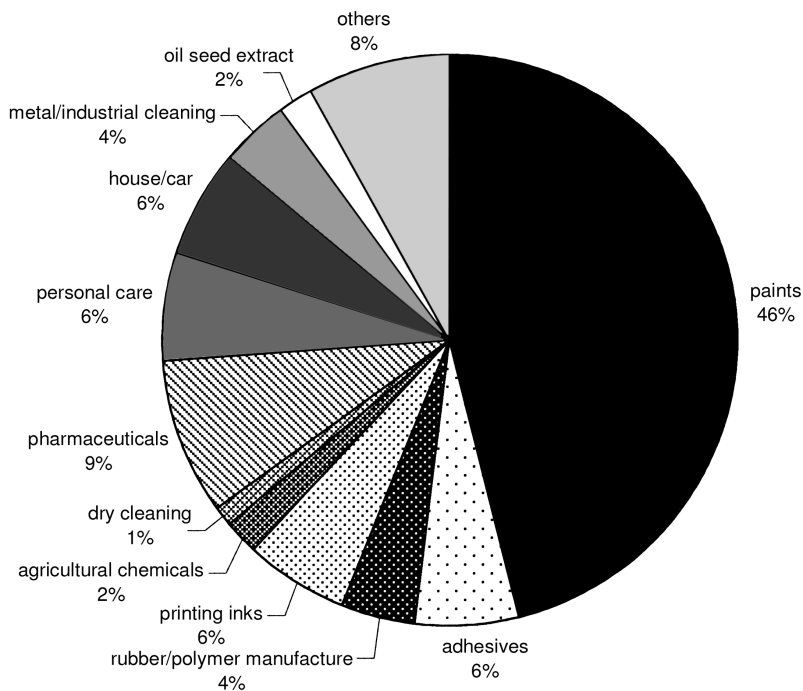
Fig. 1.2 Annual European solvent sales: 5 million tonnes, for which rubber and polymer manufacture accounts for 56% [4].

(VOCs). Approx. 20 million tonnes of VOCs are emitted into the atmosphere each year as a result of industrial activities [3]. According to Fig. 1.2, the annual European solvent sales to the rubber and polymer manufacturing industries, including polymer industries such as paints and adhesives, amount to 2.8 million tonnes.

Based on these facts, it is highly desirable from an environmental, safety, and economical point of view to develop alternative routes to reducing the use of organic solvents in polymer processes. Two obvious solutions to the organic solvents problem are the development of solvent-free processes and the replacement of solvents by environmentally benign products. Solvent-free polymerizations generally suffer from processing difficulties as a result of increased viscosities and mass transfer limitations, for instance in melt phase polymerization [5]. Solvent replacement, on the other hand, although it prevents the loss of dangerous organic solvents, still necessitates an energy-intensive solvent removal step. Using a "volatile" solvent makes the solvent removal step relatively easy. An intermediate solution is using one of the reactants in excess, as a result of which it partly acts as a solvent or plasticizer. In this case the excess of reactant still needs to be removed. Again, this becomes easier when the reactant involved is more volatile or, even better, gaseous.

Currently, the possibilities of green alternatives to replace organic solvents are being explored for a wide variety of chemical processes.

1.2
Strategic Organic Solvent Replacement

Solvents that have interesting potential as environmentally benign alternatives to organic solvents include water, ionic liquids, fluorous phases, and supercritical or dense phase fluids [5, 6]. Obviously, each of these approaches exhibits specific advantages and potential drawbacks. Ionic liquids (room-temperature molten organic salts), for example, have a vapor pressure that is negligible. Because they are non-volatile, commercial application would significantly reduce the VOC emission. In general, ionic liquids can be used in existing equipment at reasonable capital cost [7]. Nevertheless, the cost of a room-temperature molten salt is substantial. In addition, the separation of ionic liquids from a process stream is another important point of concern.

With respect to dense phase fluids, supercritical water has been shown to be a very effective reaction medium for oxidation reactions [8, 9]. Despite extensive research efforts, however, corrosion and investment costs form major challenges in these processes because of the rather extreme operation conditions required (above 647 K and 22.1 MPa) [10]. Still, several oxidation processes for waste water treatment in chemical industries are based on supercritical water technology (see, e.g., [11]).

In Table 1.1, the critical properties of some compounds which are commonly used as supercritical fluids are shown. Of these, carbon dioxide and water are the most frequently used in a wide range of applications. The production of polyethylene in supercritical propane is described in a loop reactor [13]. Supercritical ethylene and propylene are also applied, where they usually act both as a solvent and as the reacting monomer. In the field of polymer processing, the Dow Chemical Company has developed a process in which carbon dioxide is used to replace chlorofluorocarbon as the blowing agent in the manufacture of polystyrene foam sheet [14, 15].

Table 1.1 Critical conditions of several substances [12].

Solvent	T_c (K)	P_c (MPa)	Solvent	T_c (K)	P_c (MPa)
Acetone	508.1	4.70	Hexafluoroethane	293.0	3.06
Ammonia	405.6	11.3	Methane	190.4	4.60
Carbon dioxide	304.1	7.38	Methanol	512.6	8.09
Cyclohexane	553.5	4.07	*n*-hexane	507.5	3.01
Diethyl ether	466.7	3.64	Propane	369.8	4.25
Difluoromethane	351.6	5.83	Propylene	364.9	4.60
Difluoroethane	386.7	4.50	Sulfur hexafluoride	318.7	3.76
Dimethyl ether	400.0	5.24	Tetrafluoromethane	227.6	3.74
Ethane	305.3	4.87	Toluene	591.8	41.1
Ethylene	282.4	5.04	Trifluoromethane	299.3	4.86
Ethyne	308.3	6.14	Water	647.3	22.1

The interest in CO_2-based processes has strongly increased over the past decades. Fig. 1.3 shows the number of papers and patents that have been published over the years concerning polymerizations in supercritical carbon dioxide ($scCO_2$). In the last ten years, a substantial rise in publications can be observed, which illustrates the increasing interest in $scCO_2$ technology for polymer processes.

Carbon dioxide is considered to be an interesting alternative to most traditional solvents [17, 18] because of its practical physical and chemical properties: it is a solvent for monomers and a non-solvent for polymers, which allows for easy separation. To a somewhat lesser extent, it can also be a sustainable source of carbon [19]. The use of CO_2 as a reactant is considered to contribute to the solution of the depletion of fossil fuels and the sequestration of the greenhouse gas CO_2. One example in this area is the copolymerization of carbon dioxide with oxiranes to aliphatic polycarbonates [19–22].

Since *sustainability* is expected to become the common denominator of all polymer processes [23], it is important to consider this topic in relation to supercritical fluids, and $scCO_2$ in particular. To develop sustainable processes, process intensification is essential. The following requirements have been defined to be important for process intensification [24–26]:

- to match heat and mass transfer rates with the reaction rate,
- to enhance selectivity and specificity of reactions,
- to have no net consumption of auxiliary fluids,
- to achieve a high conversion of raw material,
- to improve product quality.

The present status of the sustainability of chemical processes in general has recently been reviewed [27]. Although there have been remarkable gains in energy effectiveness for the chemical industry both in Europe and the USA, it is a necessity to introduce sustainable development priorities in chemical engineering
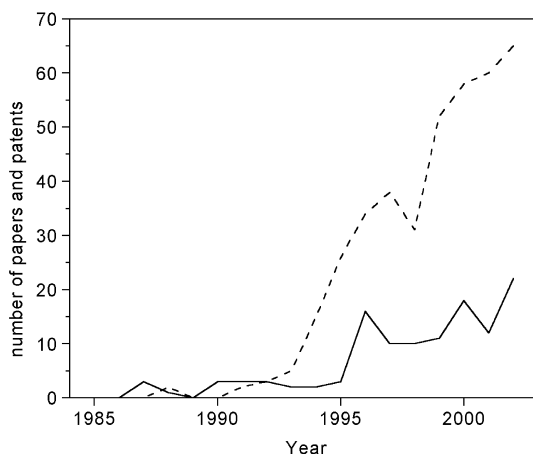
Fig. 1.3 Number of publications concerning polymerization in $scCO_2$; papers (dashed line), patents (solid line) [16].
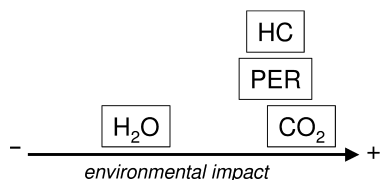
Fig. 1.4 Relative environmental impact of four dry cleaning technologies on a system level [35].

education in order to cope with future challenges. Moreover, new methodologies and design tools are being developed to implement the theme of sustainability in the conceptual process design of chemical process innovation, as illustrated in Fig. 1.4 [28].

Closely related to sustainability is the term *green chemistry*, which is defined as the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and applications of chemical products [6, 29, 30]. Life-cycle assessment (LCA) has been shown to be a useful tool to identify the more sustainable products and processes [31–33], including an environmental assessment of organic solvents as reported by Hellweg et al. [34]. The LCA-comparison of four dry cleaning technologies, i.e. based on perchloroethylene (PER), hydrocarbon (HC), wet-cleaning (H$_2$O), and liquid CO$_2$ [35], including a wide range of scientifically-based and known environmental impacts, forms an interesting case study. Based on the tendencies in the results, the wet-cleaning process does not look favorable as compared to the other three technologies (see Fig. 1.4). Various LCA studies emphasize that each specific process has to be considered individually, including analysis on energy consumption, emissions, material consumption, risk potential, and toxicity potential [33]. It is impossible to discuss in general whether polymer processes based on supercritical CO$_2$ can be sustainable or not.

Nevertheless, it is evident that the chemical process industry has to comply with regulatory issues and more stringent quality demands, which necessitates focusing on green chemistry and green engineering. Therefore, there is an increasing demand for innovative products and processes. In the past, polymer reaction engineering (PRE) was strongly based on engineering sciences. Currently, the focus is changing toward an integrated, multidisciplinary approach that is strongly driven by sustainability [36]. In the near future, a changeover will occur from technology-based PRE toward product-inspired PRE, for which it is expected that supercritical technology will play an important role [37].

1.3
Physical and Chemical Properties of Supercritical CO$_2$

In 1822, Baron Cagniard de la Tour discovered the critical point of a substance in his famous cannon barrel experiments [38]. Listening to discontinuities in the sound of a rolling flint ball in a sealed cannon, he observed the critical tem-

perature. Above this temperature, the distinction between the liquid phase and the gas phase disappears, resulting in a single supercritical fluid phase behavior. In 1875, Andrews discovered the critical conditions of CO_2 [39]. The reported values were a critical temperature of 304.05 K and a critical pressure of 7.40 MPa, which are in close agreement with today's accepted values of 304.1 K and 7.38 MPa. In the early days, supercritical fluids were mainly used in extraction and chromatography applications. A well-known example of supercritical fluid extraction is caffeine extraction from tea and coffee [40]. Supercritical chromatography was frequently used to separate polar compounds [41, 42]. Nowadays, an increasing interest is being shown in supercritical fluid applications for reaction, catalysis, polymerization, polymer processing, and polymer modification [43]. More detailed historical overviews are given by Jessop and Leitner [12] and by McHugh and Krukonis [40].

A supercritical fluid is defined as a substance for which the temperature and pressure are above their critical values and which has a density close to or higher than its critical density [44–46]. Above the critical temperature, the vapor-liquid coexistence line no longer exists. Therefore, supercritical fluids can be regarded as "hybrid solvents" because the properties can be tuned from liquid-like to gas-like without crossing a phase boundary by simply changing the pressure or the temperature. Although this definition gives the boundary values of the supercritical state, it does not describe all the physical or thermodynamic properties. Baldyga [47] explains the supercritical state differently by stating that on a characteristic microscale of approximately 10–100 Å, statistical clusters of augmented density define the supercritical state, with a structure resembling that of liquids, surrounded by less dense and more chaotic regions of compressed gas. The number and dimensions of these clusters vary significantly with pressure and temperature, resulting in high compressibility near the critical point.

To illustrate the "hybrid" properties of supercritical fluids, Table 1.2 gives some characteristic values for density, viscosity, and diffusivity. The unique properties of supercritical fluids as compared to liquids and gases provide opportunities for a variety of industrial processes.

In Fig. 1.5, two projections of the phase behavior of carbon dioxide are shown. In the pressure-temperature phase diagram (Fig. 1.5 a), the boiling line is observed, which separates the vapor and liquid regions and ends in the critical point. At the critical point, the densities of the equilibrium liquid phase and the saturat-

Table 1.2 Comparison of typical values of physical properties of gases, supercritical fluids and liquids [48], where ρ, η and $\mathcal{D}$ stand for density, viscosity and diffusivity, respectively.

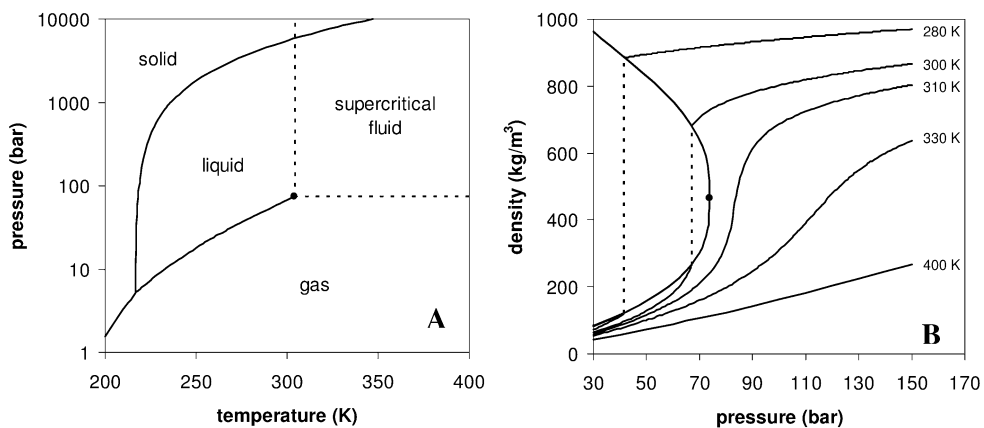| Properties	Gas	Supercritical fluid	Liquid
ρ (kg m^{-3})	1	100–800	1000
η (Pa s)	0.001	0.005–0.01	0.05–0.1
$\mathcal{D}$ (m^2 s^{-1})	$1 \cdot 10^{-5}$	$1 \cdot 10^{-7}$	$1 \cdot 10^{-9}$

Fig. 1.5 Schematic phase diagram for a pure CO$_2$. (a) The critical point at the critical temperature, T_{cr}, and the critical pressure, P_{cr}, marks the end of the vapor-liquid equilibrium line and the beginning of the supercritical fluid region. (b) Density of CO$_2$ as a function of pressure at different temperatures (solid lines) and at the vapor-liquid equilibrium line (dashed line) [44, 45].

ed vapor phases become equal, resulting in the formation of a single supercritical phase. This can be observed in the density-pressure phase diagram (Fig. 1.5 b). The transition from the supercritical state to liquid CO$_2$ is illustrated in Fig. 1.6.

In general, supercritical carbon dioxide can be regarded as a viable alternative solvent for polymer processes. Besides the obviously environmental benefits, supercritical carbon dioxide has also desirable physical and chemical properties
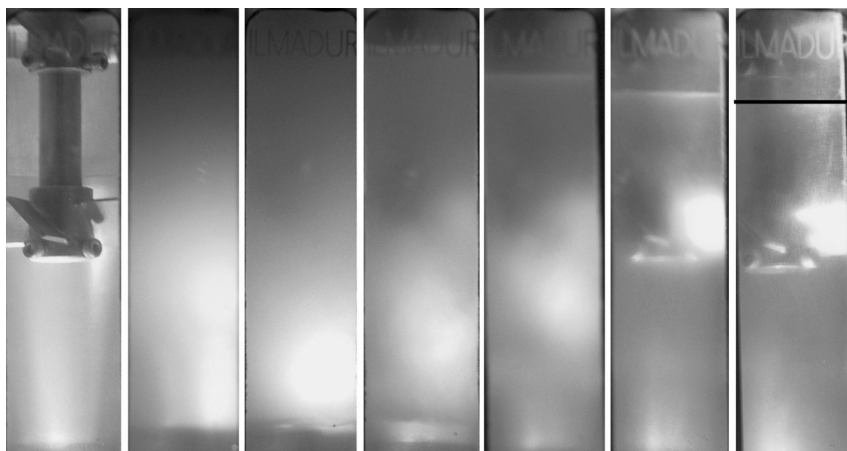

Fig. 1.6 Transition from the supercritical state to liquid CO$_2$. The line indicates the liquid-vapor interface.

scCO$_2$ + monomers, catalyst

monomers
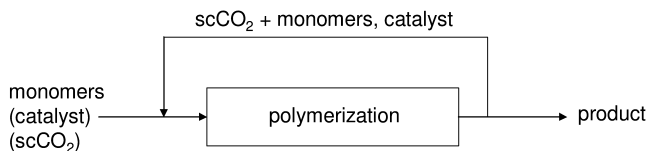(catalyst) ⟶ │ polymerization │ ⟶ product
(scCO$_2$)

Fig. 1.7 Schematic view of a catalytic polymerization based on CO$_2$
technology, in which the catalyst and monomers can be recycled
in a closed-loop process.

from a process point of view. These include its relatively chemical inertness, readily accessible critical point, excellent wetting characteristics, low viscosity, and highly tunable solvent behavior, facilitating easy separation. The use of such a "volatile" solvent makes the solvent removal step relatively easy. In principle, this allows for a closed-loop polymer process, in which the components like catalyst and monomers can be recycled. Fig. 1.7 schematically illustrates the efficiency of a CO$_2$-based polymerization as compared to a conventional process shown in Fig. 1.1.

Moreover, supercritical carbon dioxide is a non-toxic and non-flammable solvent with a low viscosity and high diffusion rate and no surface tension. A drawback of CO$_2$, however, is that only volatile or relatively non-polar compounds are soluble, as CO$_2$ is non-polar and has low polarizability and a low dielectric constant, as discussed in Section 1.4.

1.4
Interactions of Carbon Dioxide with Polymers and Monomers

For application of supercritical CO$_2$ as a medium in polymer processes, it is important to consider its interactions with polymers and monomers. In general, the thermodynamic properties of pure substances and mixtures of molecules are determined by intermolecular forces acting between the molecules or polymer segments. By examining these potentials between molecules in a mixture, insight into the solution behavior of the mixture can be obtained. The most commonly occurring interactions are dispersion, dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole (Fig. 1.8).

For small molecules, the contribution of each interaction to the intermolecular potential energy $\Gamma_{ij}(r,T)$ is given by the polarizability α, the dipole moment μ, the quadruple moment Q, and in some cases specific interactions such as complex formation or hydrogen bonding [49]. The interactions work over different distances, with the longest range for dispersion and dipole interactions. Note that the dispersion interaction depends on the polarizability only and not on the temperature. Consequently, an increased polarizability of the supercritical solvent is expected to decrease the pressures needed to dissolve a nonpolar solute or polymer. Furthermore, at elevated temperatures, the configurational
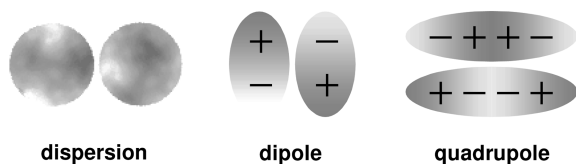
dispersion   **dipole**   **quadrupole**

Fig. 1.8 Charge distributions for various molecular interactions.

alignment of directional interactions as dipoles or quadrupoles is disrupted by the thermal energy, leading to a nonpolar behavior. Hence, it may be possible to dissolve a nonpolar solute or a polymer in a polar supercritical fluid. However, to obtain sufficient density for dissolving the solutes at these elevated temperatures, substantially higher pressures need to be applied. Additionally, specific interactions such as complex formation and hydrogen bonding can increase the solvent strength of the supercritical fluid. These interactions are also highly temperature sensitive.

The solvent strength of carbon dioxide for solutes is dominated by low polarizability and a strong quadrupole moment (Table 1.3). Consequently, carbon dioxide is difficult to compare to conventional solvents because of this ambivalent character. With its low polarizability and nonpolarity, carbon dioxide is similar to perfluoromethane, perfluoroethane, and methane.

In general, carbon dioxide is a reasonable solvent for small molecules, both polar and nonpolar. With the exception of water, for many compounds, including most common monomers, complete miscibility can be obtained at elevated pressures. However, the critical point of the mixture, i.e. the lowest pressure at a given temperature where CO_2 is still completely miscible, rises sharply with increasing molecule size. Consequently, most larger components and polymers exhibit very limited solubility in carbon dioxide. Polymers that do exhibit high solubility in carbon dioxide are typically characterized by a flexible backbone and high free volume (hence a low glass transition temperature T_g), weak interactions between the polymer segments, and a weakly basic interaction site such

Table 1.3 Physical properties of various solvents [48–50], where α is the polarizability, μ is the dipole moment and Q is the quadrupole moment.

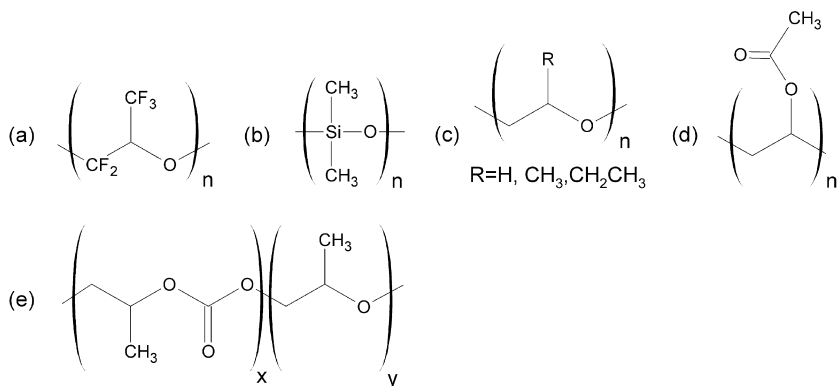| Solvent	$\alpha \cdot 10^{25}$ (cm³)	μ (D)	$Q \times 10^{26}$ (erg$^{1/2}$cm$^{5/2}$)
Methane	26	0.0	
Ethane	45.0	0.0	−0.7
Ethyne	33.3	0.0	+3.0
Hexafluoroethane	47.6	0.0	−0.7
Carbon dioxide	27.6	0.0	−4.3
n-hexane	118.3	0.0	
Methanol	32.3	1.7	
Acetone	63.3	2.9	

Fig. 1.9 Polymeric structures soluble in scCO$_2$. (a) Perfluoropoly(propylene oxide), (b) polydimethylsiloxane, (c) poly(ethylene, propylene and butylene oxide), (d) polyvinylacetate, (e) poly(ether carbonate).

as a carbonyl group [51–54]. Carbon dioxide-soluble polymers incorporating these characteristics include, e.g., polyalkene oxides, perfluorinated polypropylene oxide, polymethyl acrylate, polyvinyl acetate, polyalkyl siloxanes, and polyether carbonate (Fig. 1.9).

Although the solubility of polymers in CO$_2$ is typically very low, the solubility of carbon dioxide in many polymers is substantial. The sorption of carbon dioxide by the polymers and the resulting swelling of the polymer influence the mechanical and physical properties of the polymer. The most important effect is plasticization, i.e. the reduction of the T_g of glassy polymers. The plasticization effect, characterized by increased segmental and chain mobility as well as an increase in interchain distance, is largely determined by polymer-solvent interactions and solvent size [55]. The molecular weight of the polymer is of little influence on the swelling once the entanglement molecular weight has been exceeded.

The interaction of CO$_2$ and polymers can be divided into three application areas: processing of swollen or dissolved polymers and applications where carbon dioxide does not interact with the polymer. An extensive review on polymer processing using supercritical fluids has been written by Kazarian [55], including possible applications based on the specific interaction of CO$_2$ and the polymer system involved.

Obviously, the sorption and swelling of polymers by CO$_2$ are crucial effects in designing polymer processes based on high-pressure technology, because important properties such as diffusivity, viscosity, glass transition, melting point, compressibility, and expansion will change. The plasticization effect of CO$_2$ facilitates mass transfer properties of solutes into and out of the polymer phase, which leads to many applications: increased monomer diffusion for polymer synthesis, enhanced diffusion of small components in polymers for impregnation and extraction purposes, polymer fractionation, and polymer extrusion.

Another important requirement for the development of new polymer processes based on $scCO_2$ is knowledge about the phase behavior of the mixture involved, which enables the process variables to be tuned properly to achieve maximum process efficiency. Determining parameters in the phase behavior of a system are the solvent quality, the molecular weight, chain branching, and chemical architecture of the polymer, as well as the effect of endgroups and the addition of a cosolvent or an antisolvent. An overview of the available literature on the phase behavior of polymers in supercritical fluids has been published by Kirby and McHugh [50]. In addition, the possibilities of carbon dioxide as a medium for polymerization reactions and polymer processing have been reviewed [56–60].

1.5
Concluding Remarks and Outlook

A steady stream of emerging technologies has brought carbon dioxide all the way from a potential alternative solvent in the early 1970s to its use in industry [61]. The most promising applications of supercritical fluids are those in which their unusual properties can be exploited for manufacturing products with characteristics and specifications that are difficult to obtain by other processes.

Although there have been many interesting developments over the past twenty years, technical issues sometimes seem to hinder the progress of certain new processes toward commercialization [37, 62]. Applying carbon dioxide as a clean solvent in polymer processes is not the simplest route, because it involves, amongst others complications, high-pressure equipment, complex phase behavior, new measurement techniques, and the development of novel process concepts rather than extending conventional technologies. The development trajectory (see Fig. 1.10) from the concept idea via the laboratory bench and pilot scale to industrial implementation is often long. Currently, there exists a lack of facilities between laboratory scale research (5–500 mL) and the industrial scale application, mainly caused by the absence of pilot scale facilities. To break down the boundaries between the academic approach and industrial practice, close collaboration between industrial R & D, research institutes, and universities is essential to reduce costs, to exploit existing know-how and experimental facilities, and to reduce the development time. Bearing in mind the economics of an emerging technology as compared to long existing processes, it is a challenge to implement new process concepts at reasonable costs. For these reasons, the number of large-scale industrial polymer processes based on supercritical fluids will be limited in the short term. However, stimulation from government and research consortia should contribute substantially to the progress of development.

Several process design calculations [64, 65] have shown that polymer processes based on $scCO_2$ technology can be economically feasible, depending on the value of the product and the process conditions. Moreover, further developments will reduce costs of supercritical application substantially. It is expected that the major application of supercritical carbon dioxide will first be in the food
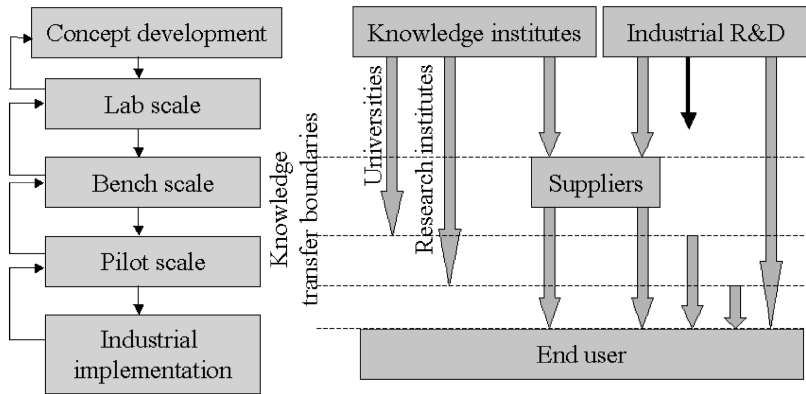
Fig. 1.10 Development trajectory of an emerging technology [63].

and pharmaceuticals industry because of additional marketing advantages, such as the GRAS (generally regarded as safe) status. However, the fact that DuPont is commercializing the production of fluoropolymers in $scCO_2$ [66] illustrates the application possibility of supercritical fluid technology in polymer processes also. In addition, the long-existing ldPE tubular process (ca. 250 MPa, 600 K) proves that a high-pressure polymerization process performed on a large scale can survive in a highly competitive field.

Nevertheless, the progress made in research today will enable the development of sustainable industrial polymer processes for the future. For this reason, the various subjects in this book have been addressed from an engineering point of view. The book is divided into three parts: an overview of polymer fundamentals, polymerization reactions, and polymer processing in supercritical carbon dioxide. It covers topics in a multidisciplinary approach starting in Part I with thermodynamics (Chapter 2), mass and heat transfer (Chapter 3), polymerization kinetics (Chapter 4), and monitoring (Chapter 5). In Part II, different types of polymerization processes (Chapters 6 to 9) will be discussed, and Part III describes the possibilities for polymer post-processing (Chapters 10 and 11), including reactive extrusion (Chapter 12), end group modification (Chapter 13), and residual monomer removal (Chapter 14).

Notation

P_c	critical pressure	[MPa]
Q	quadrupole moment	[$erg^{1/2}$ $cm^{5/2}$]
T_c	critical temperature	[K]
T_g	glass transition temperature	[K]
a	polarizability	[cm^3]
Γ_{ij}	potential energy	[J]

μ	dipole moment	[D]
ρ	density	[kg m^{-3}]
$\mathcal{D}$	diffusivity	[m^2 s^{-1}]
η	viscosity	[Pa s]
σ	surface tension	[N m^{-1}]

References

1 International Institute of Synthetic Rubber Producers, Inc., Internet publication, http://www.iisrp.com/WebPolymers/01FinalPolybutadieneVer2.pdf.

2 Condensed Course on Polymer Reaction Engineering, **2002**, *September 24–26*, Eindhoven University of Technology, The Netherlands.

3 D. T. Allen, D. R. Shonnard, *Green Engineering, Environmentally conscious design of chemical processes*, Prentice Hall PTR, Upper Saddle River, **2002.**

4 European Solvents Industry Group, http://www.esig.info/solvents_usesbenefits_details.php.

5 J. M. DeSimone, *Science*, **2002**, *297*, 799.

6 P. T. Anastas, *Green chemistry as applied to solvents*, in *Clean solvents alternative media for chemical reactions and processing*, eds.: M. A. Abraham, L. Moens, ACS Symposium Series 819, Washington, **2002.**

7 J. F. Brennecke, E. J. Maginn, *AIChE J.*, **2001**, *47*(11), 2384.

8 M. Modell, US Patent 4338199, **1982.**

9 T. B. Thomason, M. Modell, *Hazard Waste*, **1984**, *1*(4), 453.

10 T. M. Hayward, I. M. Svishchev, R. C. Makhija, *J. Supercritical Fluids*, **2003**, *27*, 275.

11 J. W. Griffith, D. H. Raymond, *Waste Management*, **2002**, *22*, 453.

12 W. Leitner, P. G. Jessop, *Chemical synthesis using supercritical fluids*, Wiley-VCH, Weinheim, **1999.**

13 A. Ahvenainen, K. Sarantila, H. Andtsjo, *WO Patent 92/12181*, **1992.**

14 G. C. Welsh, US Patent 5266605, **1993.**

15 G. C. Welsh, US Patent 5250577, **1993.**

16 SciFinder Scolar 2002, http://www.cas.org/SCIFINDER/SCHOLAR/index.html.

17 E. J. Beckman, *J. Supercritical Fluids*, **2004**, *28*, 121.

18 K. P. Johnston, R. M. Lemert, *Supercritical fluid technology: theory and applications*, in: *Encyclopedia of Chemical Processes and Design*, ed.: J. J. McKetta, Marcel Dekker, New York, **1996.**

19 D. J. Darensbourg, M. W. Holtecamp, *Coordination Chemistry Reviews*, **1996**, *153*, 155.

20 S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. B: Polymer Lett.*, **1969**, *7*, 287.

21 H. Sugimoto, S. Inoue, *J. Polym. Sci. A*, **2004**, *42*, 5561.

22 W. J. van Meerendonk, R. Duchateau, C. E. Koning, G. M. Gruter, *Macromolecular Rapid Commun.*, **2004**, *25*, 382.

23 Th. Meyer, J. T. F. Keurentjes, *Polymer reaction engineering, an integrated approach*, in *Handbook for polymer reaction engineering*, eds.: Th. Meyer, J. T. F. Keurentjes, Wiley-VCH, Weinheim, **2005.**

24 C. Ramshaw, *Chem. Eng.*, **1985**, *415*, 30.

25 A. I. Stankiewicz, J. A. Moulijn, *Chem. Eng. Prog.*, **2000**, *96*, 22.

26 R. Jachuck, *Process intensification for green chemistry*, in *Handbook of Green Chemistry & Technology*, eds.: J. Clark, D. Macquarrie, Blackwell Publishing, Oxford, **2002.**

27 R. J. Batterham, *Chem. Eng. Sci.*, **2003**, *58*, 2167.

28 G. Korevaar, *Sustainable chemical processes and products, new design methodology and design tools*, Ebrun Academic Publishers, Delft, **2004.**

29 P. T. Anastas, J. C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, Oxford, **2000.**

30 M. Lancaster, *Principles of sustainable and green chemistry*, in *Handbook of Green Chemistry & Technology*, eds.: J. Clark, D. Macquarrie, Blackwell Publishing, Oxford, **2002.**

31 M. Stewart, O. Jolliet, *Int. J. LCA*, **2004**, *9*, 153.

32 D. W. Pennington, J. Potting, G. Finnveden, E. Lindeijer, O. Jolliet, T. Rydberg, G. Rebitzer, *Environ. Int.*, **2004**, *30*, 721.

33 P. Saling, A. Kicherer, B. Dittrich-Krämer, R. Wittlinger, W. Zombik, I. Schmidt, W. Schrott, S. Schmidt, *Int. J. LCA*, **2002**, *4*, 203.

34 S. Hellweg, U. Fischer, M. Scheringer, K. Hungerbühler, *Green Chem.*, **2004**, *6*, 418.

35 P. H. Flückiger, *The use of life-cycle assessment and product risk assessment within application development of chemicals, a case study of perchloroethylene use in dry cleaning*, PhD thesis, Swiss Federal Institute of Technology Zürich, **1999**.

36 Th. Meyer, J. T. F. Keurentjes, *Trans. IChemE A*, **2004**, *82(A12)*, 1.

37 E. J. Beckman, *Ind. Eng. Chem. Res.*, **2003**, *42*, 1598.

38 C. Cagniard de la Tour, *Ann. Chim. Phys.*, **1822**, *22*, 127.

39 T. Andrews, *Proc. R. Soc.*, **1875**, *24*, 455.

40 M. A. McHugh, V. J. Krukonis, *Supercritical fluid extractions: principles and practice*, 2nd edn., Butterworth-Heinemann, Stoneham, MA, **1994.**

41 T. A. Berger, *J. Chromatogr. A*, **1997**, *785*, 3.

42 G. O. Cantrell, J. A. Blackwell, *J. Chromatogr. A*, **1997**, *782*, 237.

43 C. A. Eckert, B. L. Knutson, P. G. Debenedetti, *Nature*, **1996**, *383*, 313.

44 S. Angus, B. Armstrong, K. M. de Reuck, *International Thermodynamic Tables of the Fluid State. Carbon Dioxide*, Pergamon Press, Oxford, **1976**.

45 R. Span, W. Wagner, *J. Phys. Chem. Ref. Data*, **1996**, *25*, 1509.

46 J. A. Darr, M. Poliakoff, *Chem. Rev.*, **1999**, *99*, 495.

47 J. Baldyga, M. Henczka, B. Y. Shekunov, *Fluid dynamics, mass transfer and particle formation in supercritical fluids*, in Supercritical fluid technology for drug product development, eds.: P. York, U. B. Kompella, B. Shekunov, Marcel Dekker, New York, **2004.**

48 R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases and Liquids*, 4th edn., McGraw-Hill, New York, **1987.**

49 J. M. Prausnitz, R. N. Lichtenthaler, E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd edn., Prentice-Hall, Englewood Cliffs, **1986.**

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

51 F. Rindfleisch, T. P. DiNoia, M. A. McHugh, *J. Phys. Chem.*, **1996**, *100*, 15581.

52 T. Sarbu, T. Styranec, E. J. Beckman, *Ind. Eng. Chem. Res.*, **2000**, *39*, 1678.

53 T. Sarbu, T. Styranec, E. J. Beckman, *Nature*, **2000**, *405*, 165.

54 S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta, C. A. Eckert, *J. Am. Chem. Soc.*, **1996**, *118*, 1729.

55 S. G. Kazarian, *Polym. Sci., Ser. C*, **2000**, *42(1)*, 78.

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

57 K. A. Shaffer, J. M. DeSimone, *Trends Polym. Sci.*, **1995**, *3(5)*, 146.

58 J. L. Kendall, D. A. Canelas, J. L. Young, J. M. DeSimone, *Chem. Rev.*, **1999**, *99*, 543.

59 A. I. Cooper, *J. Mater. Chem.*, **2000**, *10*, 207.

60 M. F. Kemmere, *Recent developments in polymer processes*, in *Handbook for polymer reaction engineering*, eds.: Th. Meyer, J. T. F. Keurentjes, Wiley-VCH, Weinheim, **2005.**

61 D. Adam, *Nature*, **2000**, *407*, 938.

62 L. Chordia, R. Robey, *Proceedings of the 5th International Symposium on Supercritical Fluids*, Atlanta, **2000.**

63 J. M. K. Timmer, *Development of large scale applications (Workshop): Application of high-pressure carbon dioxide in polymer processes*, Eindhoven University of Technology, **2003.**

64 G. Brunner, *Nato Science Ser. E, Appl. Sci.*, **2000**, *366*, 517.

65 M. F. Kemmere, M. H. W. Cleven, M. A. van Schilt, J. T. F. Keurentjes, *Chem. Eng. Sci.*, **2002**, *57*, 3929.

66 G. Parkinson, *Chem. Eng.*, **1999**, *106*, May, 17.