

초임계 유체를 이용한 고분자 합성 연구

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Synthesis of Polymers in Supercritical Carbon Dioxide

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요약: 본 총설에서는 이산화탄소에 용해력이 있는 새로운 탄화수소 공중합체의 설계와 개발, 그리고 생체친화성 고분자의 초임계 중합을 위한 효과적인 계면활성제로써의 성능에 대해 소개하고, 초임계 유체의 기본적 개념을 용매로서의 성질과 고분자 합성분야에서의 응용적인 측면에서 기술한다. 이산화탄소에 높은 용해력을 지닌 탄화수소 고분자 중합을 위해 새로운 리빙라디칼 중합기술을 사용하였고, 이 물질들의 이산화탄소 내에서의 상거동을 측정하여 공중합체의 분자량과 구조가 용해도에 미치는 영향을 조사하였다. 초임계 분산중합에서의 효과적인 계면활성력을 확인하였고, 성장하는 입자의 안정화에 필요한 키 파라미터를 결정하기 위해 다양한 조건에서 실험을 수행하였으며, 화장품 분야에 응용될 수 있는 새로운 구조의 친환경 고분자 소재 개발에 이 연구가 적용될 수 있다는 잠재적인 가능성을 확인하였다.

Abstract: This review shows the design and the development of new CO₂-soluble hydrocarbon copolymers which can be used as effective stabilizers for successful dispersion polymerizations of bio-compatible materials in supercritical carbon dioxide (scCO₂). The basic concepts of supercritical fluid including its solvent properties and applications in polymer synthesis are described. We report the facile synthesis of highly soluble hydrocarbon based copolymers, prepared with good control via controlled free radical polymerization from readily accessible and commercially available monomers. The phase behaviour of these materials was monitored in pure CO₂ to investigate how the molecular weights and the composition of the copolymers affect their solubility in CO₂. Their activity as a stabilizer was then tested in dispersion polymerization of N-vinyl pyrrolidone in CO₂ at various reaction conditions to identify the key parameters required for a successful dispersion stabilization of growing PVP particles. Some prospective potentials of this research which can be applied in developing new polymer materials in an environmentally-friendly fashion for use in cosmetics are also discussed.

Keywords: supercritical, polymer, surfactant, hydrocarbon, RAFT

1. Introduction

ScCO₂ has drawn a great attention in the polymer industry as a potential medium for polymer synthesis and processing[1-8]. This is not only because of the environmental benign properties of scCO₂, but also be-

cause polymers can be prepared in this medium with novel properties that cannot be achieved via conventional organic solvents. There are three major benefits that linked the use of scCO₂ to polymer manufacture. First, polymer can be recovered as a dry product from a reaction mixture by simple depressurization. This eliminates the energy-intensive drying procedures often required in polymer synthesis to remove solvent resi-

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dues from the final product[3]. It also produces 'clean' and solvent-free materials with no contamination, which is important for use in biomedical applications[4]. Secondly, the adjustable density of scCO₂ has a significant effect in assisting the separation of the final polymer from starting materials or the simple fractionation of targeted polymer. For example, by reducing the pressure of a polymer/scCO₂ solution, the specific molecular weights of polymer fractions can be precipitated and collected independently[9,10]. Finally, high diffusivity of scCO₂ makes it possible for the CO₂ molecules to penetrate through the polymer chains. This leads to the plasticization of a wide range of polymers and also reduces the polymer's glass transition temperature (T_g) at ambient temperature[1,11,12]. This lowers the energy required for chain rotation and as a consequence the polymer substrate is liquefied. The diffusion of scCO₂ into polymers has been studied by a number of research groups and plasticization effect has been examined in a variety of polymer substrates, including PS[13], PMMA[14], PVAc[15], poly(methyl acrylate) (PMA)[16] and polycarbonates[17]. The plasticization effect of scCO₂ has proved to be very useful particularly in many polymer-processing techniques such as polymer blending and impregnation[2,4]. In addition, plasticization has been utilized in the preparation of a wide range of porous materials and foams[4, 11,18,19].

This review mainly focuses on the use of scCO₂ in polymer synthesis. ScCO₂ has been used as an alternative medium for a range of polymer syntheses including metal catalysed[20,21] and enzyme catalyzed ring-opening polymerizations[22]. The scCO₂ is particularly useful for free radical polymerization as the medium is chemically inert and therefore does not interfere with the chain transfer reactions which can affect the final molecular weight[23-25]. It has been successfully used by DuPont to produce poly(tetrafluoroethylene) (also known as Teflon®) in a precipitation polymerization, replacing CFCs[26]. According to DuPont, this scCO₂ technology produces Teflon with enhanced performance and processing capabilities, while generating less waste. It was developed jointly by

DuPont and the professor Joseph DeSimone at The University of North Carolina, Chapel Hill. The products are being manufactured at the company's plant (in Fayetteville, NC, USA) using a new 40 million US\$ facility that started up in late 2000. In certain polymerization reactions, the highly plasticized state of a polymer in CO₂ can be very favorable for enhancing the diffusion of monomer into the growing polymer product[27]. Pure scCO₂ has been reported to be a good solvent for a wide variety of monomers and initiators [28-30]. However, it is a very poor solvent for most high molecular weight polymers[31,32] or highly polar compound[33]. In order to investigate the potential use of scCO₂ in polymer synthesis there needs to be a good understanding about its ability to function as an effective polymerization medium.

2. Solvent Properties of scCO₂

There have been numerous studies into the nature of interactions between CO₂ and solutes over the last decade, but there are still a lot of questions on parameters that govern solubility in this medium[3,33]. Carbon dioxide has a low dielectric constant and behaves very similarly to a hydrocarbon with respect to its ability to dissolve small organic molecules. CO₂ also has a large quadrupole moment and acts as a weak Lewis acid that allows it to participate in polar interactions. Its dipole-quadrupole and quadrupole-quadrupole moments may assist CO₂ to dissolve some small polar molecules such as methanol[32,34,35]. A number of researchers have reported the solvating power of scCO₂ in comparison with those of toluene[36], n-hexane[37] and acetone[36]. These various parameters, which are still not clearly elucidated, make it difficult to define the solvating power of a solvent whose properties strongly depend on temperature and pressure of the system.

The main drawback with regard to polymer synthesis is that it is an extremely poor solvent for high molecular weight polymers. For example, poly(ethylene) with a molecular weight of $M_w \sim 109,000$ g/mol was found to be insoluble in scCO₂ up to temperatures of 200 °C and pressures of $\sim 40,000$ psi[38]. Another

example is PMMA: A sample with a molecular weight of 93,300 g/mol was reported to be insoluble in scCO₂ even at a temperature of 255 °C and a pressure of ~ 37,000 psi[39]. On the other hand, there are two exceptional groups of polymers, which are amorphous fluorinated polymers[34,35,40-45] and silicones[46-50]. They tend to demonstrate superior solubility in scCO₂ under mild conditions (< 100 °C, < 1000 psi). These compounds have been used as surfactants and stabilizers for dispersion polymerization of various monomers in scCO₂.

There have been several investigations to improve the miscibility of polymers in scCO₂ using certain functional groups. Dardin *et al.* have shown that specific van der Waals interactions exists between CO₂ and fluorinated materials using *in situ* high-pressure ¹H and ¹⁹F Nuclear Magnetic Resonance (NMR) spectroscopy[51]. In the case of silicone polymers, it is thought that good solubility is ascribed to the large free volumes which are created by high chain flexibility of these materials[31,52]. Another important interaction is Lewis acid-Lewis base interaction between CO₂ molecules and compounds containing electron donating groups (*e.g.* polyethers and polyesters), which was identified by Fourier Transform Infra-Red (FTIR) spectroscopy[53-56].

Homogeneous polymerizations in scCO₂ are very limited[57,58]. The first example was introduced by DeSimone *et al.* who demonstrated the successful synthesis of high molecular weight fluoropolymers in scCO₂ via homogeneous solution polymerization[59]. This process has now been commercially scaled up by DuPont to produce such fluorinated materials in large quantities[60]. In this case, a homogeneous technique can be used due to the high solubility of the fluorinated polymers in the scCO₂ continuous phase[45].

Although scCO₂ is able to dissolve a wide range of conventional vinyl monomers, the resulting polymers have limited solubility in CO₂ and therefore precipitate out of the system at relatively low molecular weights. For this heterogeneous system, the dispersion polymerization technique has become particularly useful for conducting free radical polymerizations in this me-

dium[1,3,4].

3. Dispersion Polymerization in scCO₂

As with free radical dispersion polymerization in conventional solvent, when scCO₂ is used as the reaction medium, polymerizations begin as a homogeneous mixture of monomer, initiator and scCO₂. Once the reaction takes place, polymer chains grow until they reach the critical length, and then they precipitate out of solution forming primary particles. Experimental results suggest that particle nucleation is complete very soon after a polymerization commences (before 0.1 % conversion of monomer)[61]. After the nucleation, the particle number density is maintained to be constant throughout the reaction, without forming new polymer particles[62]. The primary polymer particles need to be stabilized by a suitable surfactant to avoid aggregation of the product and to achieve high monomer conversions[63].

The stabilizers used for conventional media have been examined in terms of their solubility in CO₂ before they were actually employed in dispersion polymerization conducted in scCO₂. In 1990, Consani and Smith demonstrated a screening of the solubility of over 130 traditional stabilizers in scCO₂ at 50 °C and 1450 ~ 7250 psi[64]. They found out that these stabilizers form microemulsions much more readily in less polar SCFs, such as alkanes or xenon, rather than in scCO₂. In order to conduct a dispersion polymerization in scCO₂, a polymeric type of stabilizer is required which must possess a portion that is highly soluble in the scCO₂ phase. The design and development of such materials is intensively being studied and a variety of successful CO₂ soluble stabilizers have already been reported[1,3,4].

As with the conventional stabilizers used in organic media, those found to function effectively in scCO₂ consist of a component that is soluble in the scCO₂ continuous phase (*e.g.* a fluorinated polymer or silicone) and a polymer-philic anchor component which spreads out from the surface of the polymer particle into SCF (Figure 1).

The major hurdle in the design of new CO₂-compa-

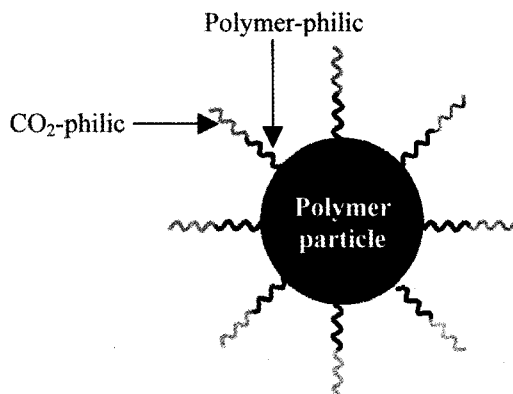


Figure 1. An illustration of the required components within a stabilizer for use in $scCO_2$.

tible stabilizers is to find high molecular weight polymers which have good CO_2 -philicity. Fluorinated polymers show high solubility in CO_2 and have been extensively used as dispersing agents during the 1990s[1, 63,65-68]. These CO_2 -soluble stabilizers have been synthesized with various types of topology and their stabilizing ability has been broadly investigated in dispersion polymerizations conducted in CO_2 [11,61,63,65, 69-78]. When a suitable surfactant such as poly(FOA) and PDMS-mMA is used, free-flowing powder particles with well-defined spherical morphology can be obtained in dispersion polymerization in CO_2 . For example, dispersion polymerization of MMA in CO_2 in the presence of poly(FOA) showed good control of morphology, producing discrete PMMA particles in a high yield (90 %)[69] (Figure 2).

Along with PMMA, there are other vinyl monomers which have been successfully polymerized in $scCO_2$ using dispersion polymerization. A collection of these monomers having a variety of pendent functional groups are shown in Figure 3.

These vinyl monomers include acrylonitrile[80,81], styrene[82-84], vinylidene fluoride[85-87], vinyl acetate[88,89], methyl methacrylate[75,90,91], poly(ethylene glycol) methacrylate[92], 1-vinyl-2-pyrrolidone [93], glycidyl methacrylate[94,95], 2-(dimethyl-amino)ethyl methacrylate[96], 2-hydroxyethyl methacrylate[97,98], and isobornyl methacrylate[92]. In all cases, the polymer product was recovered without solvent residue and in high yield.

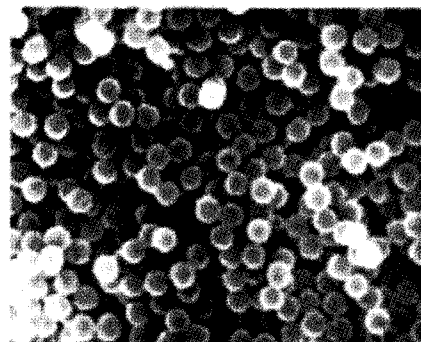


Figure 2. SEM image of PMMA particles synthesized with 0.47 % of poly(FOA). $M_n = 259\,000$ g/mol, PDI = 2.53, Yield = 90% and particle size diameter = 1.01[69].

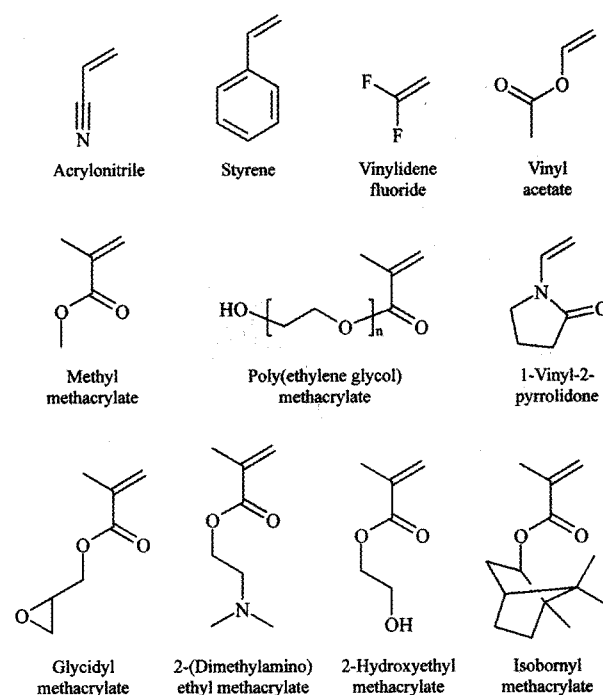


Figure 3. The selection of monomers which have been successfully polymerized by dispersion polymerizations in $scCO_2$ [79]. These vinyl monomers include: acrylonitrile [80,81], styrene[82-84], vinylidene fluoride[85-87], vinyl acetate[88,89], methyl methacrylate[75,90,91], poly(ethylene glycol) methacrylate[92], 1-vinyl-2-pyrrolidone [93], glycidyl methacrylate[94,95], 2-(dimethyl-amino)-ethyl methacrylate[96], 2-hydroxyethyl methacrylate[97, 98], and isobornyl methacrylate[92].

However, the use of fluorinated polymers to prepare CO_2 philic stabilizers is relatively expensive[99]. A reactive silicone (methacrylate terminated polydimethyl

siloxane) was also applied as a stabilizer in the polymerization of MMA in $scCO_2$, but its performance was not as effective as the fluorinated polymers[100]. Ultimately, stabilizers containing fluorine and silicone are not likely to be applied industrially.

Given this background, the design of new hydrocarbon-based surfactants has emerged as one of the greatest challenges in $scCO_2$ technologies. The design and development of a CO_2 -philic hydrocarbon polymer with solubility comparable to that of fluorocarbons would allow production of surfactants 10 ~ 100 times less expensive than their fluorinated counterparts[101]. It is suggested that the identification of highly CO_2 -soluble polymers composed of only carbon, hydrogen, and oxygen could facilitate the design of safe, inexpensive, environmentally benign " CO_2 -philes" and therefore enhance the performance and commercial success of CO_2 -based technologies[56].

4. Hydrocarbon Surfactants

Recently, hydrocarbons substituted with carbonyl groups have been regarded as economical, environmentally friendly CO_2 -philic materials. Particularly, poly(vinyl acetate) has been recognized as the most CO_2 -philic hydrocarbon material thanks to its relatively higher solubility in CO_2 than any other hydrocarbon homopolymers[56]. Several publications attribute this to the favorable specific interactions between CO_2 and the acetate groups in PVAc. It was indicated by *Ab initio* molecular orbital calculations that the interaction between the carbonyl groups of acetate functional groups and CO_2 is almost half as strong as the hydrogen bond interaction in a water dimer[102]. This specific interaction between CO_2 and carbonyl groups has been confirmed by IR spectroscopic studies[53]. In addition, it has been shown that a weak, but cooperative C-H...O hydrogen bond, involving the hydrogen atom attached to the carbonyl carbon and one of the oxygen atoms in CO_2 , reinforces the Lewis acid-Lewis base interactions [103]. Figure 4 represents the two cooperating interactions.

Based on this background, Woods *et al.* [104] first

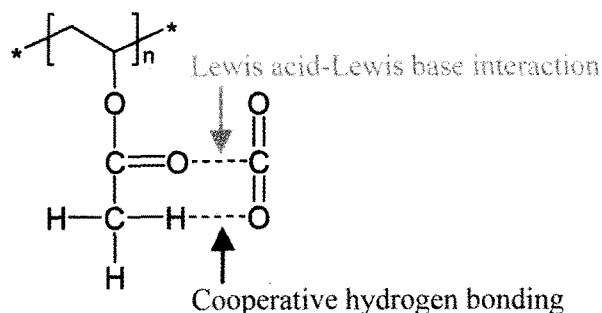


Figure 4. Illustration of the interactions between PVAc and CO_2 .

investigated the use of PVAc as the CO_2 -philic portion in the design of hydrocarbon surfactants. In this work, VAc was copolymerized with several different methacrylate monomers to synthesize statistical copolymer stabilizers incorporating PVAc CO_2 -philic portions (Figure 5). Their solubility in pure CO_2 and in a mixture of CO_2 /MMA was measured and their stabilizing ability was examined in terms of copolymer architecture.

Out of all these PVAc based copolymers investigated, the most successful copolymer stabilizer used in a dispersion polymerization of MMA in $scCO_2$ was found to be PVAc-PCMO (85:15) (Figure 5(a)) producing a PMMA product with high molecular weight ($M_w > 250,000$ g/mol) in good yield (90 %). The PMMA product was obtained in the form of white powder with an average particle size of 5 μm (Figure 6).

However, it was found that this excellent result was not 100 % reproducible during further experiments using PVAc-PCMO from both the same batch and a new batch synthesized in the same way. It was suggested that the free radical copolymerization employed for the synthesis of PVAc-PCMO allows limited control over the final copolymer architecture and this has proved to be problematic in reproducing successful results[104].

Despite the poor reproducibility of this copolymer stabilizer, this work has established a prospective platform for further development of hydrocarbon surfactants for use in $scCO_2$ technologies.

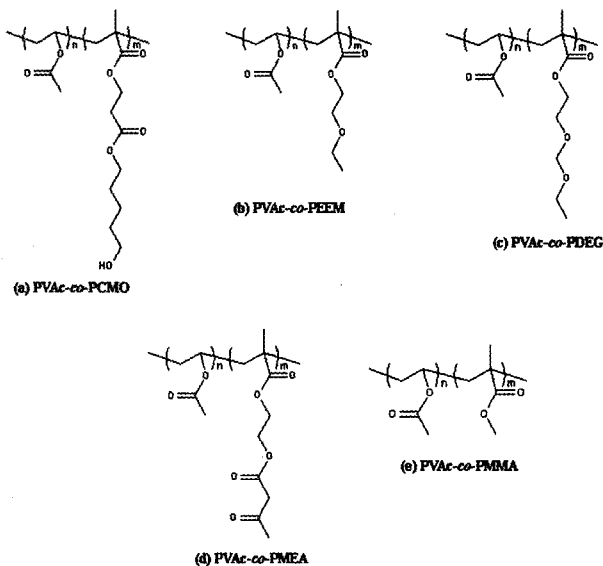


Figure 5. PVAc-based statistical copolymers prepared by free radical polymerization of VAc with different methacrylate co-monomers[104]. CMO = caprolactone 2-(methacryloyloxy) ethyl ester, EEM = 2-ethoxyethyl methacrylate, DEG = di(ethylene glycol) ethyl ether methacrylate, MEA = 2-(methacryloyloxy) ethyl acetoacetate, MMA = methyl methacrylate.

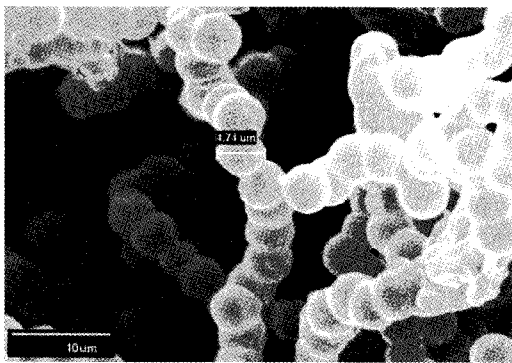


Figure 6. SEM image of PMMA product polymerized in the presence of PVAc-PCMO (85:15)[104].

5. Controlled Synthesis of Hydrocarbon Copolymers via RAFT

A major problem associated with PVAc-based polymers is that VAc is particularly difficult to polymerize in a controlled way. VAc lacks a conjugating substituent and as a result its propagating radical is highly reactive, less stable and tends to undergo chain transfer

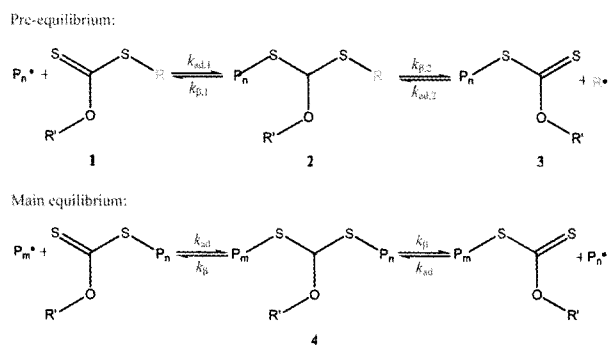
and termination reactions[105]. Eventually, the molecular weight of PVAc products can be difficult to predict and polydispersity tends to be high. Presently, VAc cannot be polymerized easily by metal mediated living radical polymerization - one reason is that it is difficult to generate radical species from dormant PVAc-halogen terminals[106]. This is thought to be a result of the weakly electron donating acetyl substituent in VAc, which prevents dormant PVAc-halogen species from receiving an electron from the metal catalyst. It has been found that a side reaction occurs involving the decomposition of the dormant PVAc-halogen terminal.

As a result of the difficulties associated with controlling the radical polymerization of VAc, the preparation of PVAc copolymers with well-defined architecture is highly challenging and examples are scarce in the literature[107-111].

5.1. Reversible Addition Fragmentation Chain Transfer (RAFT)

The RAFT process has proved to be the method of choice for successfully mediating VAc polymerization[112,113]. Xanthates especially have been found to effectively control vinyl acetate polymerizations. RAFT polymerization with xanthates is sometimes called MADIX (Macromolecular Design by Interchange of Xanthate)[113,114].

When using xanthates as mediating agents, in which the stabilizing Z-groups are $-OR'$, an enhanced electron density on the central carbon effectively decreases the stability of the intermediate RAFT radicals **2** and **4** (see Scheme 1), hence, counterbalancing the instability of the growing vinyl ester radicals. Moreover, the addition rates of the propagating radicals toward **1** and **3** are decreased, due to a resonance stabilization that lowers the double-bond character of the C=S bond in **1** and **3**. If the addition-fragmentation reaction is fast compared to propagation, the typical features of a "living" radical polymerization are obtained, that is, a linear increase in the number-average molecular weight M_n with conversion and a low polydispersity[115].



Scheme 1. Basic reaction steps of the RAFT process employing xanthates as mediating agents[116].

Stenzel *et al.*[117] investigated the ability of a set of eight xanthates to induce living characteristics in free radical vinyl acetate polymerization with respect to molecular weight control and kinetic behaviour. They reported that all suitable xanthates induced extended periods of inhibition and moderate rate retardation. It is also suggested that the ability of the compounds to control VAc polymerization can be correlated with the electron density on the central carbon atom of the xanthate.

A particular type of xanthate, *O*-ethylxanthyl ethyl propionate (Figure 7), bearing an ethyl propionate leaving group (R) was purposely designed for this study. To produce such a xanthate, a selective one-pot synthesis using TCDI (1,1'-thiocarbonyl diimidazole) was employed. This strategy introduced by Perrier *et al.*[118] presents clear advantages in terms of yield, reaction time, and simplicity for the synthesis of chain transfer agents for RAFT or MADIX polymerization.

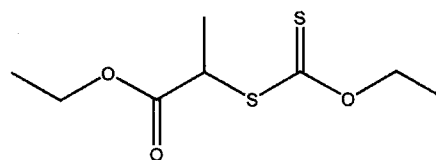


Figure 7. Structure of *O*-ethylxanthyl ethyl propionate.

5.2. Synthesis of Hydrocarbon Copolymers

Hydrocarbon copolymers of vinyl acetate and vinyl butyrate (PVAc-PVB-X) with different molecular weights were synthesized using xanthate as a RAFT agent. The molecular weights were targeted to range from 2,000 g/mol to 10,000 g/mol because, in general, hydrocarbon polymers with molecular weights above 10,000 g/mol have very poor solubility in scCO₂[119] Table 1 summarizes the properties of the 50:50 random copolymers of PVAc-PVB-X.

M_n determined by GPC shows good agreement with theoretical molecular weight $M_{n,th}$ indicating good control over the molecular weights of copolymers. PDIs tend to increase as the molecular weights increase, which is similar behaviour to that observed for homopolymers.

The actual composition ratio calculated by ¹H NMR (Figure 8) was very close to the initial feed ratio of each monomer. This proves that each of the monomer radicals equally undergoes addition and fragmentation process with the xanthate (non-selective, non-competing sequence). The monomer conversion was very high (> 93 %).

Table 1. The Copolymerization of Vinyl Esters using Xanthate as a RAFT Agent

Entry	Polymer	Feed Ratio	Final Ratio ^{b)}	M:R:I ^{a)}	Conv. ^{b)} (%)	$M_{n,th}$ (g/mol)	M_n (GPC) (g/mol)	PDI
1	PVAc-PVB-X	50:50	49:51	20:1:0.1	99	2200	2400	1.29
2	PVAc-PVB-X	50:50	49:51	30:1:0.1	99	3200	3600	1.43
3	PVAc-PVB-X	50:50	48:52	40:1:0.1	99	4200	4000	1.45
4	PVAc-PVB-X	50:50	48:52	80:1:0.1	97	8000	8600	1.77
5	PVAc-PVB-X	50:50	50:50	108:1:0.1	99	10900	10800	1.75
6	PVAc-PVB-X	50:50	50:50	148:1:0.1	99	14900	14900	1.81

Reaction conditions: at 65 °C for 48 h

a) M:R:I=Monomer : RAFT (xanthate) : Initiator (AIBN), b) Determined by ¹H NMR data

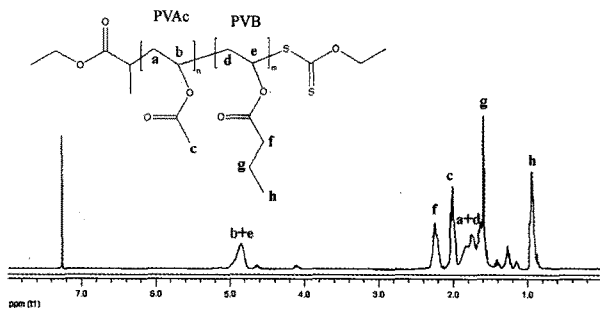


Figure 8. ^1H NMR of PVAc-PVB-X.

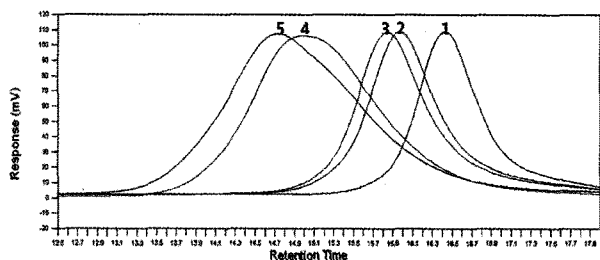


Figure 9. GPC traces for PVAc-PVB-X copolymerization in the presence of xanthate (Table 1, Entry 1: $M_n = 2,400$ g/mol, PDI = 1.29; Entry 2: $M_n = 3,600$ g/mol, PDI = 1.43; Entry 3: $M_n = 4,000$ g/mol, PDI = 1.45; Entry 4: $M_n = 8,600$ g/mol, PDI = 1.77; Entry 5: $M_n = 10,800$ g/mol, PDI = 1.75).

The copolymers were obtained as viscous liquid or sticky solid. The lower the molecular weight, the more yellow the colour of the polymers because the amount of xanthate (the colour of which is yellow) required for the synthesis of lower molecular weight product is relatively larger. GPC chromatographs of the vinyl ester copolymers with various molecular weights are shown in Figure 9.

5.3. Solubility of Hydrocarbon Surfactants in scCO_2

The solubility of hydrocarbon copolymers prepared in this work has been compared to other CO_2 soluble polymers (Figure 10).

Poly(vinyl ester) polymers show the greatest solubility of any hydrocarbons in scCO_2 reported to date, which is comparable to the cloud point curves for PDMS-mMA (10,000 g/mol) and hydroxyl-terminated Krytox (4,800 g/mol); the two most common surfactants used in scCO_2 . Although the solubility of the poly(vinyl ester) hydrocarbon polymers is still lower

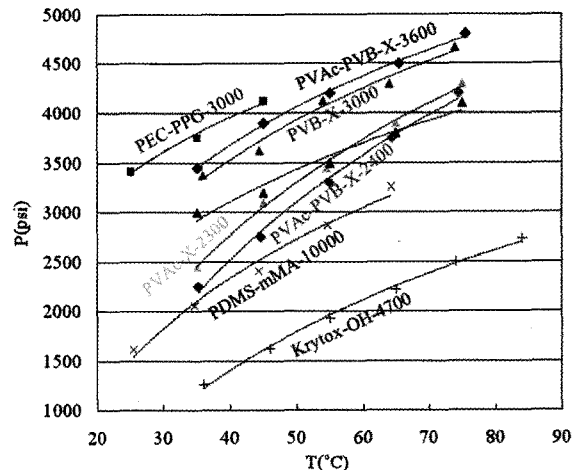


Figure 10. The cloud point curves (recorded in pure CO_2) for PVAc-X, PVB-X, PVAc-PVB-X (50:50), PEG-PPG-3000[119], PDMS-mMA and Krytox-OH.

than that of the commercially available surfactants (based on absolute molecular weight comparisons), all the cloud points are well below 5,000 psi at all useful temperatures for free radical polymerization.

Furthermore, the cloud point pressures for the most soluble polymer reported until now (synthesized by Cooper *et al.*[119]) were also plotted. They showed a significantly higher cloud point than all of the poly(vinyl ester) polymers. Indeed, all of the copolymers prepared by xanthate using vinyl acetate and vinyl butyrate were found to be much more soluble in scCO_2 than that of PEC-PPG-3000[119].

6. Dispersion Polymerization of PVP in scCO_2

Poly(vinyl pyrrolidone), also known as PVP, is a unique bio-compatible polymer as it provides a remarkable combination of properties such as transparency, chemical and biological inertness, very low toxicity as well as high media compatibility and crosslinkable flexibility. PVP is readily prepared by the polymerization of N-vinyl pyrrolidone (N-VP).

6.1. Dispersion Polymerization of PVP in scCO_2

Supercritical CO_2 has been successfully used as dispersing medium in the polymerization of N-VP, which cannot be synthesized by heterogeneous techniques in

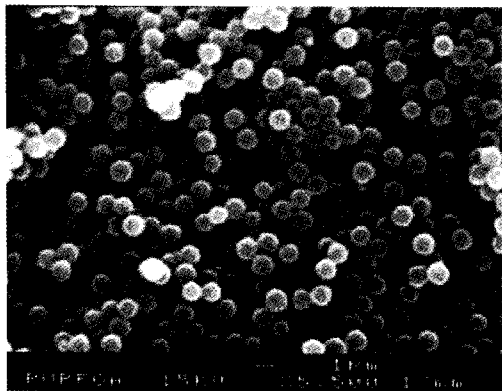


Figure 11. SEM of PVP particles synthesized with 2 wt% poly(FOA) stabilizer[93].

water-based polymerization systems. In 2000, Desimone *et al.*[93] first reported the dispersion polymerization of N-VP using low molecular weight poly (FOA) as the stabilizer. The polymerization in the presence of this surfactant produced free-flowing powders after venting CO₂. SEM revealed that the polymers consisted of micron-sized spheres with relatively narrow size distributions (Figure 11). They found out that increasing concentrations of poly(FOA) yielded a decrease in particle diameter, while increasing the monomer concentration produced an increase in particle size. No significant change was observed in the particle morphology for polymerizations conducted at different pressures.

Berger *et al.*[120] employed easily accessible and well-characterized PS-*b*-PDMS diblock copolymer surfactants to stabilize the growing PVP particles. In contrast to the polymerization without stabilizer, the reaction led to the formation of uniform microparticles in a regular spherical shape. The dispersion polymerization of N-VP in scCO₂ was found to be very sensitive to the reaction parameters, especially the concentration of stabilizer. The broad molecular weight distribution of the products differs from that of a conventional dispersion polymerization of N-VP. They interpreted this by a surface plasticization of the growing particles leading to inhomogeneous polymerization conditions.

Galia *et al.*[121] studied the batch free radical polymerization of N-VP in CO₂ in the presence of a reactive polysiloxane surfactant (PDMS-*m*MA). They investigated the effect of the concentration of the sur-

face active macromonomer, the initiator and the monomer, and the effect of the density of the fluid phase on the kinetics of the process and on the morphology of the particles. From the collected experimental results, they strongly suggested that the polymerization of N-VP in the presence of PDMS-*m*MA could proceed with a nucleation mechanism different from that postulated in pure dispersion polymerization stabilized by graft-forming surfactants.

The studies shown above has proven that PVP (either as homopolymer or as copolymer with other vinyl monomer) can be synthesized in supercritical CO₂ using a suitable surfactant. However, CO₂ soluble surfactants required to stabilize the growing PVP polymer particles have been limited to costly fluorinated polymer (poly(FOA)) or siloxane based polymers (PDMS-*m*MA, PS-*b*-PDMS)[122]. The aim of our work was to extend this research and see if the hydrocarbon poly(vinyl ester) polymers synthesized above could act as very effective stabilizers for dispersion polymerization reactions in scCO₂.

6.2. Stabilizing Ability of Hydrocarbon PVAc-PVB-X Copolymer

The stabilizing ability of RAFT-terminated hydrocarbon copolymers of vinyl ester (PVAc-PVB-X) was examined in dispersion polymerization of N-vinyl pyrrolidone (N-VP) in CO₂. In order to look at the effect of the molecular weights of the stabilizer, the low molecular weight PVAc-PVB-X-2400 was firstly tested at the concentration of 5 wt% wrt monomer with AIBN as an initiator in dispersion polymerization of N-VP in CO₂ at 65 °C. The product was obtained as a viscous liquid in low yield. The use of 10 wt% stabilizer also did not improve the monomer conversion. When the amount of AIBN was increased to twice as much, the monomer conversion slightly increased (from 0.53 to 0.73) but the product was still in the form of sticky polymer. This indicates that the low molecular weight PVAc-PVB-2400 does not have enough stabilizing activity regardless of the stabilizer concentration and initiator concentration.

In the following experiments, a new type of azo ini-

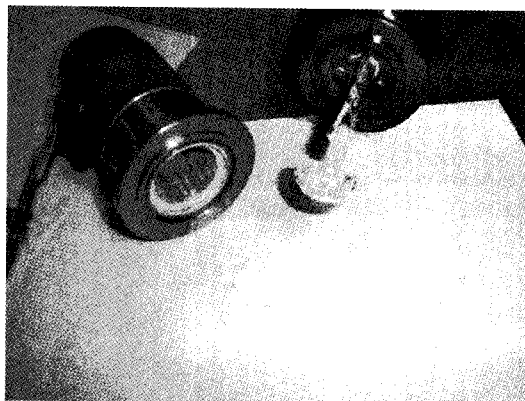
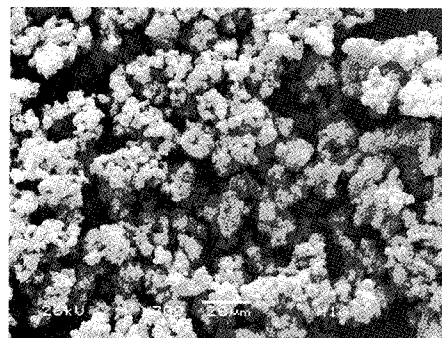


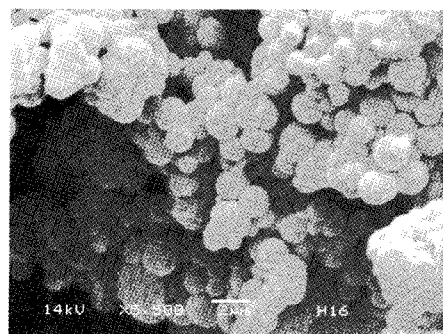
Figure 12. The free flowing powder of PVP particles obtained directly after the polymerization with 5 wt% PVAc-PVB-X8600 stabilizer in $scCO_2$.

tiator VA-70 which has a low decomposition temperature ($t_{1/2} = 10$ hours at $30\text{ }^\circ\text{C}$) was introduced to enable the polymerization in CO_2 to take place at low temperature as $35\text{ }^\circ\text{C}$ (where the density, or the solvent power of CO_2 is relatively higher). At this lower temperature, it has been observed that the stabilizers are generally more soluble in CO_2 to form a homogeneous phase at the early stage and thus provide good steric stabilization during the polymerization in CO_2 . The higher molecular weight PVAc-PVB-X-4000 was then employed with VA-70 as an initiator at $35\text{ }^\circ\text{C}$, 5,000 psi. Interestingly, the final product was not sticky but glassy material. An examination on the results from the preliminary experiments above revealed that the use of higher molecular weight considerably improved the yield and the polymer morphology. Nevertheless, their activity as stabilizers was still not good enough to produce fine microparticles.

The next stabilizer examined was PVAc-PVB-X-8600 copolymer. To a great surprise, this copolymer greatly acted as a stabilizer to achieve excellent dispersion stability. The resulting polymer was collected as a free flowing powder (Figure 12) with well defined spherical morphology (Figure 13). This was "The First Time" that the successful hydrocarbon stabilization has been achieved in supercritical CO_2 [122]. SEM analysis of the PVP polymers produced showed slightly agglomerated but spherical particles with a narrow size distribution (approximately $1\text{ }\mu\text{m}$ in diameter) (Figure 13).



(a)

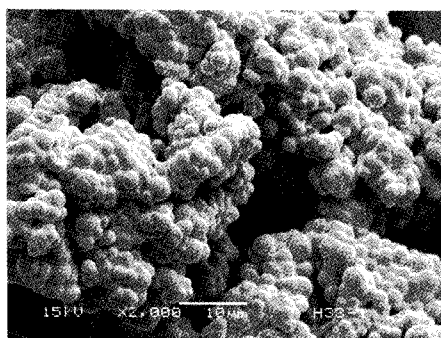


(b)

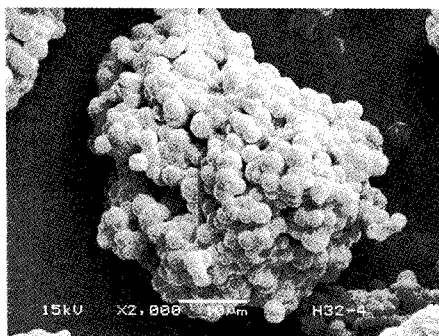
Figure 13. SEM images of PVP particles formed by dispersion polymerization in $scCO_2$ using PVAc-PVB-X-8600 as a stabilizer ((b) is the enlargement image of (a)). The particles were slightly agglomerated but mostly spherical showing a narrow size distribution (approximately $1\text{ }\mu\text{m}$ in diameter).

This slight agglomeration of PVP particles synthesized in $scCO_2$ has been previously reported by Berger *et al.*[120] They used the PS-*b*-PDMS stabilizer and obtained uniform PVP particles which were also slightly agglomerated like "glued" spheres. They interpreted this by a plasticization of the particle shells under polymerization condition. Likewise, in this study, it is assumed that a soft shell was formed in the outer sphere of the particles as a consequence of the incorporation of "soft" stabilizer molecules (T_g of PVAc-PVB-X is approximately $-1\text{ }^\circ\text{C}$ at ambient pressure). This soft shell is then plasticized and allows for the particles to fuse with one another and therefore to form aggregates.

The molecular weights ($M_w = 175,000\text{ g/mol}$) and the polydispersity ($PDI = 6.25$) was similar to those of PVP reported by Berger *et al.*[120] (where $M_w = 240,000\text{ g/mol}$, $PDI = 9.7$). This unusually high poly-



(a)



(b)

Figure 14. SEM images of PVP particles formed by dispersion polymerization in $scCO_2$ using (a) PVAc-PVB-X-10800 and (b) PVAc-PVB-X-15000 as stabilizers. Note that the particles are spherical and about 1 ~ 2 μm in diameter.

dispersity is probably ascribed to the inhomogeneous, nonstationary reaction conditions and/or a high radical transfer rate to the monomer[123].

The reactions were repeated employing the higher molecular weight stabilizers (PVAc-PVB-X-10800 and PVAc-PVB-X-15000), which also produced free flowing powders of PVP particles with quantitative polymer yields. The SEM analysis also showed a spherical shape of the particles, but some agglomeration was still seen in both products (Figure 14).

As shown above, initial experiments with low molecular weight stabilizers (PVAc-PVB-X-2400, PVAc-PVB-X-4000) were not successful and this was ascribed to the insufficient length of these chains to force steric stabilization of the dispersion. However, on increasing the PVAc-PVB-X copolymers to molecular weights greater than 8,000 g/mol and up to 15,000

g/mol, excellent dispersion stability was achieved. Polymerizations resulted in quantitative monomer conversion and well stabilized polymeric microspheres.

Interestingly, these longer surfactant chains are not soluble in pure $scCO_2$ at pressures below 5,000 psi, but they are soluble in the $scCO_2$ /monomer mixture. PVAc-PVB-X copolymer (50:50, $M_n = 15,000$ g/mol) shows a cloud point of less than 5,000 psi in the $scCO_2$ /N-VP mixture (15 wt% N-VP) at temperatures less than 50 $^{\circ}C$.

6.3. The Effect of CO_2 Density on the Dispersion Stability

The reactions were conducted to study the effect of CO_2 density varying the reaction temperature. 5 wt% of PVAc-PVB-X-10800 copolymer was used as a stabilizer. The reaction at 35 $^{\circ}C$ (at which CO_2 density is 0.950 g/mL) perfectly produced a white powder. When the reaction was conducted at 65 $^{\circ}C$ (CO_2 density is 0.841 g/mL), the product was obtained not as a powder but as an aggregated clump of polymer. This is ascribed to the poor solubility of the stabilizer in CO_2 /monomer mixture at this temperature.

This result can be clearly explained by Figure 15. The phase behaviour of PVAc-PVB-X-10800 stabilizer in CO_2 /monomer mixture was observed via variable volume view cell.

At 35 $^{\circ}C$, 5,000 psi (which is well over the cloud point curve), the stabilizer was completely dissolved in CO_2 and a transparent and homogeneous phase was seen through the view cell (Figure 15(a)). As a result, a fine powder was formed by the successful dispersion polymerization. At 65 $^{\circ}C$ and 5,000 psi (below the cloud point curve), on the contrary, the stabilizer remained undissolved and the view cell revealed an opaque phase of the mixture. Under this condition the growing particles were not stabilized, hence the polymerization resulted in poor dispersion stability producing agglomerated polymer blocks (see Figure 15(b)). These results clearly demonstrate that the CO_2 density is directly related to the solubility of stabilizer, which is the crucial factor for a perfect dispersion polymerization to be performed.

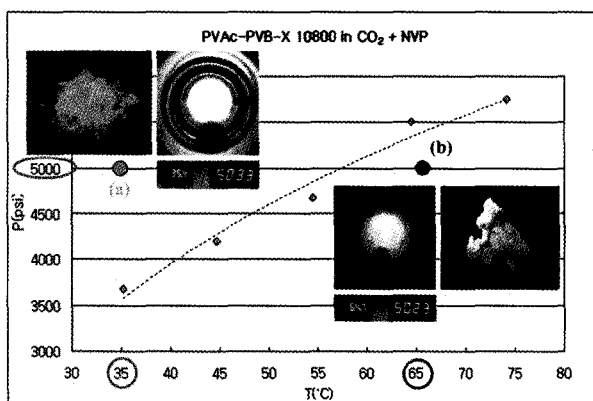


Figure 15. Cloud point curve for PVAc-PVB-X-10800, phase behaviour observation in view cell and the resulting PVP polymer by dispersion polymerization (a) at 35 °C, 5000 psi and (b) at 65 °C, 5000 psi. At 35 °C, 5000 psi (which is well over the cloud point curve), the stabilizer was completely dissolved in CO₂ and a transparent and homogeneous phase was seen through the view cell. As a result, a fine powder was formed by the successful dispersion polymerization. At 65 °C and 5000 psi (below the cloud point curve), on the contrary, the stabilizer remained undissolved and the view cell revealed an opaque phase of the mixture. Under this condition, the polymerization resulted in poor dispersion stability producing an agglomerated polymer blocks.

7. Conclusion

This review focused on the design of new CO₂-soluble hydrocarbon polymers for the use as effective stabilizers for dispersion polymerization of bio-compatible materials in supercritical CO₂. A particular type of RAFT agent, xanthate, was successfully used to facilitate excellent control over the molecular weight and polydispersity of hydrocarbon vinyl ester copolymers. The phase behaviour study proved that PVAc-PVB-X copolymers are much more soluble than any other hydrocarbon materials reported until now. We have also shown that it was possible to produce bio-compatible PVP microparticles by dispersion polymerization in scCO₂ using RAFT-terminated PVAc-PVB-X copolymers as stabilizers. The results have shown that higher density of CO₂ help to completely dissolve the stabilizers and therefore improve the dispersion stability. Dispersion polymerizations resulted in quantitative

monomer conversion and produced a free flowing powder with well defined spherical morphology. Our studies are now focused on extending this strategy to a wider range of vinyl polymerizations in scCO₂ and investigating the application of this approach into such areas as controlled synthesis of bio-macromolecules and development of new functional copolymer architectures for use in cosmetics and pharmaceuticals.

References

1. A. I. Cooper, *Journal of Materials Chemistry*, **10**(2), 207 (2000).
2. S. G. Kazarian, *Polymer Science*, **42**(1), 78 (2000).
3. J. L. Kendall, D. A. Canelas, J. L. Young, and J. M. DeSimone, *Chemical Reviews*, **99**(2), 543 (1999).
4. H. M. Woods, M. Silva, C. Nouvel, K. M. Shakesheff, and S. M. Howdle, *Journal of Materials Chemistry*, **14**(11), 1663 (2004).
5. E. J. Beckman, *Industrial & Engineering Chemistry Research*, **42**(8), 1598 (2003).
6. A. I. Cooper and J. M. DeSimone, *Current Opinion in Solid State & Materials Science*, **1**(6), 761 (1996).
7. A. I. Cooper, *Green Chemistry*, **1**(6), G167 (1999).
8. S. M. Howdle and A. I. Cooper, CO₂ Under Pressure - A Clean Solution for Polymer Processing, *Materials World*, pp. 10 ~ 12 (2000).
9. J. A. Lopes, D. Gourgouillon, P. J. Pereira, A. M. Ramos, M. N. da Ponte, *Journal of Supercritical Fluids*, **16**(3), 261 (2000).
10. S. Kim, Y. S. Kim, and S. B. Lee, *Journal of Supercritical Fluids*, **13**(1-3), 99 (1998).
11. D. L. Tomasko, H. B. Li, D. H. Liu, X. M. Han, M. J. Wingert, L. J. Lee, and K. W. Koelling, *Industrial & Engineering Chemistry Research*, **42**(25), 6431 (2003).
12. H.-P. Hentze and M. Antonietti, *Reviews in Molecular Biotechnology*, **90**, 27 (2002).
13. J. Q. Pham, K. P. Johnston, and P. F. Green, *Journal of Physical Chemistry B*, **108**(11), 3457 (2004).
14. B. L. West, S. G. Kazarian, M. F. Vincent, N. H.

- Brantley, and C. A. Eckert, *Journal of Applied Polymer Science*, **69**(5), 911 (1998).
15. Y. Sato, T. Takikawa, S. Takishima, and H. Masuoka, *Journal of Supercritical Fluids*, **19**(2), 187 (2001).
 16. R. G. Wissinger and M. E. Paulaitis, *Journal of Polymer Science Part B-Polymer Physics*, **25**(12), 2497 (1987).
 17. Y. P. Handa and Z. Y. Zhang, *Cellular Polymers*, **21**(4), 221 (2002).
 18. A. I. Cooper, *Advanced Materials*, **15**(13), 1049 (2003).
 19. A. I. Cooper, *Advanced Materials*, **13**(14), 1111 (2001).
 20. D. Bratton, M. Brown, and S. M. Howdle, *J. Polym. Sci., Part A: Polym. Chem.*, **43**(24), 6573 (2005).
 21. D. Bratton, M. Brown, and S. M. Howdle, *Macromolecules*, **38**(4), 1190 (2005).
 22. F. C. Loeker, C. J. Duxbury, R. Kumar, W. Gao, R. A. Gross, and S. M. Howdle, *Macromolecules*, **37**(7), 2450 (2004).
 23. J. M. DeSimone, E. E. Maury, Y. Z. Menceloglu, J. B. McClain, T. J. Romack, and J. R. Combes, *Science*, **265**(5170), 356 (1994).
 24. Z. Guan, J. R. Combes, Y. Z. Menceloglu, and J. M. DeSimone, *Macromolecules*, **26**(11), 2663 (1993).
 25. J. L. Kendall, D. A. Canelas, J. L. Young, and J. M. DeSimone, *Chem. Rev.*, **99**(2), 543 (1999).
 26. T. J. Romack, J. R. Combes, and J. M. DeSimone, *Macromolecules*, **28**(5), 1724 (1995).
 27. D. A. Canelas and J. M. DeSimone, *Macromolecules*, **30**(19), 5673 (1997).
 28. Y. S. T. Arai and T. Takebayashi, *Supercritical Fluids: Molecular Interactions, Physical Properties and New Applications*. Springer: Berlin (2002).
 29. J. A. Darr and M. Poliakoff, *Chemical Reviews*, **99**(2), 495 (1999).
 30. M. A. McHugh and V. J. Krukoni, *Supercritical Fluid Extraction: Principles and Practice*. Butterworth-Heinemann: Boston (1994).
 31. C. F. Kirby and M. A. McHugh, *Chemical Reviews*, **99**(2), 565 (1999).
 32. M. L. O'Neill, Q. Cao, R. Fang, K. P. Johnston, S. P. Wilkinson, C. D. Smith, J. L. Kerschner, and S. H. Jureller, *Industrial & Engineering Chemistry Research*, **37**(8), 3067 (1998).
 33. P. G. Jessop and W. Leitner, *Chemical Synthesis Using Supercritical Fluids*. Wiley-VCH: Weinheim (1999).
 34. D. A. Newman, T. A. Hoefling, R. R. Beitle, E. J. Beckman, and R. M. Enick, *Journal of Supercritical Fluids*, **6**(4), 205 (1993).
 35. C. Lepilleur, E. J. Beckman, H. Schonemann, and V. J. Krukoni, *Fluid Phase Equilibria*, **134**(1-2), 285 (1997).
 36. J. A. Hyatt, *Journal of Organic Chemistry*, **49**(26), 5097 (1984).
 37. J. M. Walsh, G. D. Ikononou, and M. D. Donohue, *Fluid Phase Equilibria*, **33**(3), 295 (1987).
 38. F. Rindfleisch, T. P. DiNoia, and M. A. McHugh, *Journal of Physical Chemistry*, **100**(38), 15581 (1996).
 39. F. Rindfleisch, T. P. DiNoia, and M. A. McHugh, *J. Phys. Chem-US*, **100**(38), 15581 (1996).
 40. T. P. DiNoia, S. E. Conway, J. S. Lim, and M. A. McHugh, *Journal of Polymer Science Part B-Polymer Physics*, **38**(21), 2832 (2000).
 41. N. Sundararajan, S. Yang, K. Ogino, S. Valiyaveetil, J. G. Wang, X. Y. Zhou, C. K. Ober, S. K. Obendorf, and R. D. Allen, *Chemistry of Materials*, **12**(1), 41 (2000).
 42. C. A. Mertdogan, T. P. DiNoia, and M. A. McHugh, *Macromolecules*, **30**(24), 7511 (1997).
 43. M. E. Wright, K. M. Lott, M. A. McHugh, and Z. H. Shen, *Macromolecules*, **36**(7), 2242 (2003).
 44. R. Enick, E. Beckman, A. Yazdi, V. Krukoni, H. Schonemann, and J. Howell, *Journal of Supercritical Fluids*, **13**(1-3), 121 (1998).
 45. G. Luna-Barcenas, S. Mawson, S. Takishima, J. M. DeSimone, I. C. Sanchez, and K. P. Johnston, *Fluid Phase Equilibria*, **146**(1-2), 325 (1998).
 46. R. Fink and E. J. Beckman, *Journal of Supercritical Fluids*, **18**(2), 101 (2000).
 47. Z. Bayraktar and E. Kiran, *Journal of Applied Polymer Science*, **75**(11), 1397 (2000).
 48. K. Liu and E. Kiran, *Journal of Supercritical Fluids*,

- 16(1), 59 (1999).
49. Y. B. Melnichenko, E. Kiran, G. D. Wignall, K. D. Heath, S. Salaniwal, H. D. Cochran, and M. Stamm, *Macromolecules*, **32**(16), 5344 (1999).
 50. Y. Xiong and E. Kiran, *Polymer*, **36**(25), 4817 (1995).
 51. A. Dardin, J. M. DeSimone, and E. T. Samulski, *Journal of Physical Chemistry B*, **102**(10), 1775 (1998).
 52. R. Fink, D. Hancu, R. Valentine, and E. J. Beckman, *Journal of Physical Chemistry B*, **103**(31), 6441 (1999).
 53. S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta, and C. A. Eckert, *Journal of the American Chemical Society*, **118**(7), 1729 (1996).
 54. J. C. Meredith, K. P. Johnston, J. M. Seminario, S. G. Kazarian, and C. A. Eckert, *Journal of Physical Chemistry*, **100**(26), 10837 (1996).
 55. C. Drohmann and E. J. Beckman, *Journal of Supercritical Fluids*, **22**(2), 103 (2002).
 56. Z. Shen, M. A. McHugh, J. Xu, J. Belardi, S. Kilic, A. Mesiano, S. Bane, C. Karnikas, E. Beckman, and R. Enick, *Polymer*, **44**(5), 1491 (2003).
 57. H. Shiho and J. M. Desimone, *J. Polym. Sci., Part A: Polym. Chem.*, **38**(7), 1139 (2000).
 58. J. R. Combes, Z. Guan, and J. M. DeSimone, *Macromolecules*, **27**(3), 865 (1994).
 59. J. M. Desimone, Z. Guan, and C. S. Elsbernd, *Science*, **257**(5072), 945 (1992).
 60. M. McCoy, *Chemical & Engineering News*, **10** (1999).
 61. M. L. O'Neill, M. Z. Yates, K. P. Johnston, C. D. Smith, and S. P. Wilkinson, *Macromolecules*, **31**(9), 2848 (1998).
 62. G. Li, M. Z. Yates, K. P. Johnston, and S. M. Howdle, *Macromolecules*, **33**(11), 4008 (2000).
 63. J. M. Desimone, E. E. Maury, Y. Z. Menciloglu, J. B. McClain, T. J. Romack, and J. R. Combes, *Science*, **265**(5170), 356 (1994).
 64. K. A. Consani and R. D. Simth, *The Journal of Supercritical Fluids*, **3**, 51 (1990).
 65. Y. L. Hsiao, E. E. Maury, J. M. Desimone, S. Mawson, and K. P. Johnston, *Macromolecules*, **28**(24), 8159 (1995).
 66. T. M. Yong, W. P. Hems, J. L. M. vanNunen, A. B. Holmes, J. H. G. Steinke, P. L. Taylor, J. A. Segal, and D. A. Griffin, *Chemical Communications*, (18), 1811 (1997).
 67. W. P. Hems, T. M. Yong, J. L. M. van Nunen, A. I. Cooper, A. B. Holmes, and D. A. Griffin, *Journal of Materials Chemistry*, **9**(7), 1403 (1999).
 68. H. Shiho and J. M. DeSimone, *Journal of Polymer Science Part a-Polymer Chemistry*, **38**(7), 1146 (2000).
 69. Y. L. Hsiao and J. M. DeSimone, *Journal of Polymer Science Part a-Polymer Chemistry*, **35**(10), 2009 (1997).
 70. D. A. Canelas, D. E. Betts, J. M. DeSimone, M. Z. Yates, and K. P. Johnston, *Macromolecules*, **31**(20), 6794 (1998).
 71. H. Shiho and J. M. DeSimone, *Journal of Polymer Science Part a-Polymer Chemistry*, **37**(14), 2429 (1999).
 72. K. K. Kapellen, C. D. Mistele, and J. M. DeSimone, *Macromolecules*, **29**(1), 495 (1996).
 73. K. A. Shaffer, T. A. Jones, D. A. Canelas, J. M. DeSimone, and S. P. Wilkinson, *Macromolecules*, **29**(7), 2704 (1996).
 74. M. L. O'Neill, M. Z. Yates, K. P. Johnston, C. D. Smith, and S. P. Wilkinson, *Macromolecules*, **31**(9), 2838 (1998).
 75. C. Lepilleur and E. J. Beckman, *Macromolecules*, **30**(4), 745 (1997).
 76. F. Rindfleisch, R. Becker, and W.-D. Hergeth, *Polymeric Materials Science and Engineering*, **80**, 518 (1999).
 77. A. I. Cooper, W. P. Hems, and A. B. Holmes, *Macromolecular Rapid Communications*, **19**(7), 353 (1998).
 78. A. I. Cooper, W. P. Hems, and A. B. Holmes, *Macromolecules*, **32**(7), 2156 (1999).
 79. A. Gregory, Controlled Polymerisations in Supercritical Carbon Dioxide. University of Nottingham, nottingham (2007).
 80. Z. Wang, Y. J. Yang, Q. Dong, T. Liu, and C. P. Hu, *Polymer*, **47**(22), 7670 (2006).
 81. H. Shiho and J. M. DeSimone, *Macromolecules*,

- 33(5), 1565 (2000).
82. D. A. Canelas, D. E. Betts, and J. M. DeSimone, *Macromolecules*, **29**(8), 2818 (1996).
83. R. Wang and H. M. Cheung, *J. Appl. Polym. Sci.*, **93**(2), 545 (2004).
84. H. Shiho and J. M. Desimone, *J. Polym. Sci., Part A: Polym. Chem.*, **38**(7), 1146 (2000).
85. H. Tai, W. Wang, and S. M. Howdle, *Macromolecules*, **38**(5), 1542 (2005).
86. J. DeSimone and L. Riddick, *Proceedings - NOB-CChE*, **26**, 53 (1999).
87. P. A. Mueller, G. Storti, M. Morbidelli, I. Costa, A. Galia, O. Scialdone, and G. Filardo, *Macromolecules*, **39**(19), 6483 (2006).
88. Y. Yang, Q. Dong, Z. Wang, C. Shen, Z. Huang, H. Zhu, T. Liu, and C. P. Hu, *J. Appl. Polym. Sci.*, **102**(6), 5640 (2006).
89. F. Rindfleisch, R. Becker, and W.-D. Hergeth, *Polym. Mater. Sci. Eng.*, **80**, 518 (1999).
90. K. A. Shaffer, T. A. Jones, D. A. Canelas, J. M. DeSimone, and S. P. Wilkinson, *Macromolecules*, **29**(7), 2704 (1996).
91. H. M. Woods, C. Nouvel, P. Licence, D. J. Irvine, and S. M. Howdle, *Macromolecules*, **38**(8), 3271 (2005).
92. M. R. Giles, R. M. T. Griffiths, D. J. Irvine, and S. M. Howdle, *Eur. Polym. J.*, **39**(9), 1785 (2003).
93. T. Carson, J. Lizotte, and J. M. Desimone, *Macromolecules*, **33**(6), 1917 (2000).
94. H. Shiho and J. M. DeSimone, *Macromolecules*, **34**(5), 1198 (2001).
95. W. Wang, R. M. T. Griffiths, A. Naylor, M. R. Giles, D. J. Irvine, and S. M. Howdle, *Polymer*, **43**(25), 6653 (2002).
96. W. Wang, M. R. Giles, D. Bratton, D. J. Irvine, S. P. Armes, J. V. W. Weaver, and S. M. Howdle, *Polymer*, **44**(14), 3803 (2003).
97. Z. Ma and P. Lacroix-Desmazes, *Polymer*, **45**(20), 6789 (2004).
98. H. Shiho and J. M. DeSimone, *J. Polym. Sci., Part A: Polym. Chem.*, **38**(20), 3783 (2000).
99. E. J. Beckman, *Chemical Communications (Cambridge, United Kingdom)*, (17), 1885 (2004).
100. A. L. C. Burke, G. Maier, and J. M. DeSimone, *Abstracts of Papers of the American Chemical Society*, 211, 152-PMSE (1996).
101. T. Sarbu, T. J. Styranec, and E. J. Beckman, *Industrial and Engineering Chemistry Research*, **39**(12), 4678 (2000).
102. M. R. Nelson and R. F. Borkman, *Journal of Physical Chemistry A*, **102**(40), 7860 (1998).
103. P. Raveendran and S. L. Wallen, *Journal of the American Chemical Society*, **124**, 7274 (2002).
104. H. M. Woods, Hydrocarbon Stabilisers for Use in Supercritical Carbon Dioxide. The University of Nottingham (2005).
105. G. S. Moad, D. H., *The Chemistry of Free Radical Polymerization*. Pergamon: Oxford (1995).
106. M. Wakioka, K.-Y. Baek, T. Ando, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **35**(2), 330 (2002).
107. D. Batt-Coutrot, D. M. Haddleton, A. P. Jarvis, and R. L. Kelly, *European Polymer Journal*, **39**(12), 2243 (2003).
108. S. H. Qin and K. Y. Qiu, *Polymer*, **42**(7), 3033 (2001).
109. Z. J. Lu, X. Y. Huang, and J. L. Huang, *Journal of Polymer Science Part a-Polymer Chemistry*, **37**(14), 2595 (1999).
110. X. Y. Huang, Z. J. Lu, and J. L. Huang, *Polymer*, **39**(6-7), 1369 (1998).
111. B. Boutevin, M. Macret, C. Maubert, Y. Pietrasanta, and M. Tanesie, *Tetrahedron Letters*, (33), 3019 (1978).
112. E. Rizzardo, J. Chiefari, R. T. A. Mayadunne, G. Moad, and S. H. Thang, *ACS Symposium Series*, **768**(Controlled/Living Radical Polymerization), 278 (2000).
113. D. Charmot, P. Corpart, H. Adam, S. Z. Zard, T. Biadatti, and G. Bouhadir, *Macromolecular Symposia*, **150**(Polymers in Dispersed Media), 23 (2000).
114. G. Moad, E. Rizzardo, and S. H. Thang, *Australian Journal of Chemistry*, **58**(6), 379 (2005).
115. W. Smulders, R. G. Gilbert, M. J. Monteiro, *Macromolecules*, **36**(12), 4309 (2003).
116. D. Boschmann and P. Vana, *Polymer Bulletin*

- (Heidelberg, Germany), **53**(4), 231 (2005).
117. M. H. Stenzel, L. Cummins, G. E. Roberts, T. P. Davis, P. Vana, and C. Barner-Kowollik, *Macromolecular Chemistry and Physics*, **204**(9), 1160 (2003).
118. M. R. Wood, D. J. Duncalf, S. P. Rannard, and S. Perrier, *Organic Letters*, **8**(4), 553 (2006).
119. B. Tan, H. M. Woods, P. Licence, S. M. Howdle, and A. I. Cooper, *Macromolecules*, **38**(5), 1691.
120. T. Berger, B. McGhee, U. Scherf, and W. Steffen, *Macromolecules*, **33**(10), 3505 (2000).
121. A. Galia, A. G., V. Iaia, and G. Filardo, *J. Polym. Sci. Pol. Chem.*, **42**, 173 (2004).
122. H. Lee, E. Terry, M. Zong, N. Arrowsmith, S. Perrier, K. J. Thurecht, and S. M. Howdle, *J. Am. Chem. Soc.*, **130**(37), 12242 (2008).
123. B. I. Bomer, *Houben-Weyl : Methoden der Organischen Chemie*. Stuttgart, Vol. E20/2 (1987).