Green Chemistry

Accepted Manuscript

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/greenchem

Green Chemistry

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Insight into the Role of Intermolecular Interactions on the Enhanced Solubility of Fluorinated Epoxide Oligomer in Supercritical CO_2

Gai-Gai Zhou[a], Jian-Gang Chen*[,a], Ming-Xi Wang[a], Min Zhang[a], Jing-Long Guo[a], Shukun Shen[b], Zhao-Tie Liu[a], Zhong-Wen Liu[a], Jinqiang Jiang[a], Jian Lu[*,c]

A prominent enhancement of solubility of epoxide oligomer in supercritical CO_2 (scCO_2) was definitely accomplished *via* fluorination. The fluorinated epoxide oligomers (FEO) exhibited incredibly low transition pressure (P_T) as compared with a library of other epoxide oligomers. For discerning the nature of the observed special affinity of the FEO to CO_2, the detailed solvation behaviors of 14 epoxide oligomers in gaseous and supercritical CO_2 were investigated using a set of high-pressure *in-situ* ATR FTIR as pressure increased from 0.1 to 40.0 MPa. The key role of the intermolecular interactions on the enhanced solubility of FEO in scCO_2 was established and major factors impacting on the molecular interplay between the epoxide oligomers and CO_2 were systematically evaluated. We attribute the uniquely enhanced solubility of FEO in scCO_2 to the synergistic effects of the increased special attraction between FEO and CO_2, the decreased self-interaction among FEO and the excellent accessibility of FEO to CO_2. Since FEO is suggested to be the most soluble species in scCO_2, we optimistically believe that FEO may act as the ideal solubilizing chain after being transplanted or grafted into some targeted molecules and thus can be employed in developing a series of novel fluorinated monomers, ligands/complexes/catalysts and surfactants in scCO_2 system.

Introduction

Supercritical carbon dioxide (scCO_2) has attracted extensive attentions for its various advantages over traditional solvents during the past decades. It is accepted as a nontoxic, nonflammable, easily recyclable and environmentally benign medium that may promisingly take the place of the environmentally harmful traditional organic solvents in many fields.[1] Moreover, the solvability or solvation power of scCO_2 can be turned by altering pressure and/or temperature without changing the composition of the system.[2] Additionally, the products are easily separated *via* decompression after the process/reaction without the detectable residual of solvent as well as volatile reactants.[3] Hence, scCO_2 is available to be applied in the fields such as homogeneous catalysis or the extraction of noble metal, in which the challenge of poor reuse or recycle of catalysts is expected to be improved.[4] While simultaneously, the barrier in the application of scCO_2 has also been clearly stated as its nonpolarity and the resulted inability to effectively solvate the majority of polar compounds,[5] macromolecules,[6] chelating ligands and catalysts containing transition metal complexes.[7] So far numerous attempts of both experimental work[5a,8] and theoretical simulation[9] have been spurred to overcome such limitation by seeking proper surfactants or solubilizers with an appropriate aggregation behavior and good solubility in scCO_2. Therefore, much attention has been paid to investigate the intermolecular interaction and its dominated solvation behaviors of certain category of dispersates which may potentially improve the solvability (*via* effectively decreasing the operation pressure) of scCO_2 system.[10]

So far numerous fluorinated organics are found to exhibit enhanced solubility in scCO_2.[11] Inspired by such discernment, a large amount of work has been performed with exciting results, in which perfluoroalkyl groups were intentionally introduced to increase the solubility of chelating ligands or organometallic catalysts/complexes in scCO_2 in the past years. For example, Wai et al. synthesized bis(trifluoroethyl) dithiocarbamate chelating agent (FDDC)[12] and several fluorinated β-diketones[13] which exhibited not only significantly higher solubility in CO_2 but also excellent extraction efficiencies to some metal ions. Besides, Kainz et al.[14] selected the long perfluoroalkyl group of $(CH_2)_2(CF_2)_yF$ (y=6, 8) as solubilizing chains for the bidentate chelating phosphane

---

[a] Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), and School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an 710119, China E-mail: jgchen@snnu.edu.cn; Tel: +86-29-81530803
[b] School of Materials Science & Engineering, Shaanxi Normal University, Xi'an 710119, China
[c] Xi'an Modern Chemistry Research Institute, Xi'an, 710065, China E-mail: lujian204@263.net; Tel: +86-29 88291213

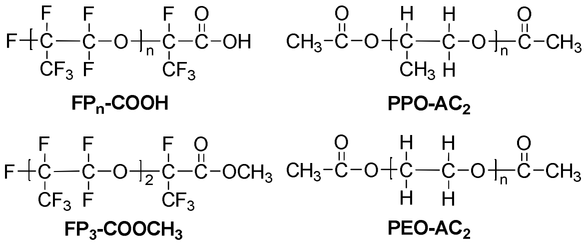
Electronic Supplementary Information (ESI) available: [FT-IR spectra of PEO-Ac_2, PEO400-Ac_2 and ^{1}H NMR spectra of PEO400-Ac_2. FT-IR spectra of PPO-Ac_2, PPO400-Ac_2 and ^{1}H NMR spectra of PPO400-Ac_2. FT-IR spectra of FP_2-$COOCH_3$, ^{1}H NMR spectra and ^{13}C NMR spectra of FP_2-$COOCH_3$. P_T of the epoxide oligomer + CO_2 systems. The reproducibility of the P_T of the epoxide oligomer + CO_2 systems]. See DOI:10.1039/x0xx00000x ligand so as to enhance the solubility of arylphosphanes and their metal complexes in $scCO_2$ without impairing their catalytic efficiency. Other researches focusing on Rh[15] or Pd[16] complexes with fluorinated phosphate ligands applied in catalytic reaction in $scCO_2$ were also reported.

It was clearly predicted that either long perfluoroalkyl group or more perfluoroalkyl groups should be expectantly introduced as solubilizing chains if enhanced/promising solubility of targeted ligands/complexes/catalysts in $scCO_2$ was expected.[12-16] While it is known that perfluoroalkyl groups were generally (or at least in main part) prepared though electrochemical (per)fluorination,[17] in which a longer chain (more hydrongen-carbon bonds) of the hydrocarbon (or its derivative) substrate has, a lower selectivity and the resulted lower yield of the product with perfluoroalkyl group obtains (since more by-products may be produced), leading to a high preparation cost and a limited application in both research and industrial field. Therefore, substances that are more soluble in $scCO_2$, environmental benign, and easily to be prepared in large scale have be the long-cherished alternative to the perfluoroalkyl solubilizing chain.

Drohmann et al. suggested that some epoxide oligomers/polyethers showed relatively high solubility in $scCO_2$, and even more so was polypropylene glycol (PPO) with non-polar groups attaching to its chain ends due to the weaker intermolecular interaction between PPO segments and the resulted lower cohesive energy density relative to the poly(ethylene glycol) analogs.[18] Thus, it seems that epoxide oligomers/polyethers may be promising or potential substitutes for the perfluoroalkyl solubilizers. Moreover, Casimiro et al found that the perfluoropolyether/ perfluoroether oligomer such as oligomer of hexafluoro-propylene oxide (PHFPO, with a number average molecular weight (M_n) of approximately 2500) exhibited considerably high solubility in CO_2 under relatively moderate conditions *via* investigating the phase behaviors of the binary system.[10b] However, neither were the impacts of molecular weight or other factors on the solubility or the phase behaviors of PHFPO in CO_2 explored, nor were the differences in the solubility between PHFPO and other non-fluorinated epoxide oligomers/polyethers compared or discussed. As a result, whether such epoxide oligomer(s) could be employed as potential solubilizing chain so far is still not elucidated.

The oligomer of hexafluoropropylene oxide/PHFPO could be prepared *via* an anionic ring-opening polymerization of hexafluoropropylene (HFPO),[10a,19] through which the long perfluoropolyether chain may be easily constructed. More importantly, HFPO oligomers with a series of molecular weights could be prepared by altering the polymerization conditions along with proper separation technology so as to meet the various needs in the research and even industrial fields with higher efficiency, better selectivity and certainly lower cost than that in the electrochemical (per)fluorination method. Therefore, the HFPO oligomers as well as the anionic polymerization method should be especially valued for the research focusing on seeking the substitute for the perfluoroalkyl solubilizers.

In the present work, the detailed solvation processes and phase behaviors of 3 categories (PEO, PPO and PHFPO (FP_n-COOH/FP_n-$COOCH_3$)) of 14 epoxide oligomers in $scCO_2$ were investigated to systematically compare the solubility of the oligomers by using a set of high pressure *in-situ* ATR FTIR system (HP ATR-FTIR). The structure of the model oligomers of epoxide used is shown in Scheme 1. By analyzing the evolution of the subtly spectral results obtained from the *in-situ* ATR-FTIR, the key role of the intermolecular interactions in the epoxide oligomer + CO_2 systems were discerned and evaluated, through which the major factors impacting on the molecular interplay and the resulted solvation behaviors of the oligomers in CO_2 were systematically illuminated. The present work is expected to provide desirable/fundamental insight as well as promising methodology into designing and developing low cost and high solubility chelating ligands/complexes, novel monomers and high efficient surfactants in $scCO_2$ system.



Scheme 1 Structure of the Model Epoxide Oligomers Used.

Results and discussion

Preparation of the oligomers of epoxide

The oligomers of PEO-Ac_2 and PPO-Ac_2 used in the present work were prepared *via* the esterification of PEO and PPO. Employing PEO400-Ac_2 and PPO400-Ac_2 as examples, the preparation as well as the characterization of the same category of the epoxide oligomers was demonstrated, as shown in Fig.s S1 and S2, respectively. As shown in Fig. S1, the strong absorption peak at 1737 cm^{-1}, attributed to the stretching vibration of the carbonyl groups (ν(C=O)) in PEO400-Ac_2, is clearly observed after the esterification (as shown in Fig. S1(B)). Simultaneously, the absorption peak around 3456 cm^{-1}, which is assigned to the stretching vibration absorption of hydroxyl group (ν(-OH))(shown in Fig. S1(A), thoroughly disappears. Thus, the hydroxyl end groups in PEO400 were completely endcapped by acetyl group. This is further verified *via* the ^1H NMR, as shown in Fig. S1(C)). The peak centered at 2.08 ppm indicates the successful introduction of the acetyl group(s) to the epoxide oligomer. Similar changes could also be found in the spectral results of PPO400-Ac_2, as shown in Fig. S2. Based on such results, we believed that the targeted epoxide oligomers of PEO-Ac_2 and PPO-Ac_2 were successfully prepared.

The oligomers of FP_n-COOH (n =1, 2, 3) were prepared *via* the hydrolysis of the corresponding FP_n-COF. The hydrolysis process was monitored *via* the HP *in-situ* FTIR system. The FTIR spectral series were shown in Fig. 1.

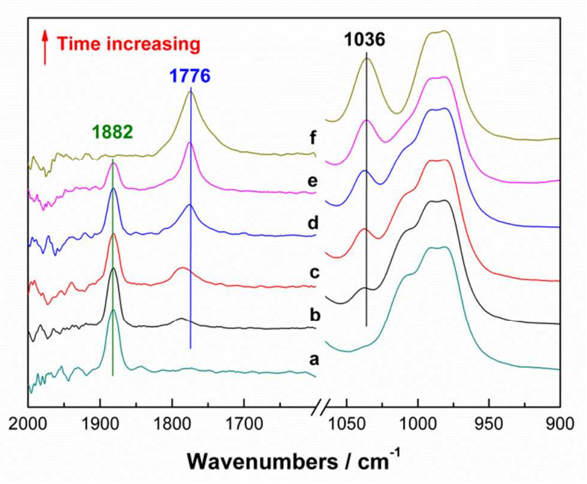


Fig. 1 *In-situ* FT-IR spectral series during the hydrolysis process of FP_3-COF. (a) 0 min; (b) 10 min; (c) 20 min; (d) 60 min; (e) 90 min; (f) 120 min. The spectral series were measured using an *in-situ* ATR-FTIR system at a room temperature. The resolution of the ATR-FTIR was 2.0 cm^{-1}. The number of scan accumulated was 8.

It is clearly shown that the absorbance of the peak centered at 1882 cm^{-1}, which is assigned to *v*(C=O) of FP_3-COF, gradually decreases with the increase of reaction time (from a to f, as shown in Fig. 1). While simultaneously, the absorbance of the peaks at 1776 cm^{-1} and 1036 cm^{-1}, assigned to the *v*(C=O) and *v*(C-O) in FP_3-COOH, respectively, is found to increasingly increase during the hydrolysis process until the absorption band of *v*(C=O) in FP_3-COF (centered at 1882 cm^{-1}) completely disappears. It is indicated that the FP_3-COOH was successfully prepared.

The oligomer of FP_3-$COOCH_3$ was prepared *via* the esterification of FP_3-COF with CH_3OH. As shown in Fig.s 1(a) and S3(A), it is clearly found that the absorption band of the *v*(C=O) dramatically shifted from 1882 to 1791 cm^{-1} during the esterification process. Since the absorption peak centered at 1791 cm^{-1} is assigned to the *v*(C=O) in FP_3-$COOCH_3$, and no detectable absorption peak(s) around 1882 cm^{-1} and/or 3300 cm^{-1} could be found, indicating that FP_3-COF was completely converted to FP_3-$COOCH_3$ (without any carboxylic acid byproduct). Moreover, as is shown in Fig. S3(B) and (C), the newly eruptive peak centered at 4.10 ppm in ^1H NMR as well as at 56.35 ppm in ^{13}C NMR also further verified the successful preparation of FP_3-$COOCH_3$.

Monitoring the intermolecular-interaction dominated solvation processes of the epoxide oligomer + CO_2 systems

It is claimed that *in-situ* FTIR is a promising and powerful tool for probing the intermolecular interactions in $scCO_2$ system.[10a,21] In the present work, a set of HP *in-situ* ATR-FTIR spectrum monitoring system was used to track the solvation and dispersion process of epoxide oligomers in gaseous and supercritical CO_2, so as to probe the detailed vibrational absorption evolution as CO_2 pressure increased. Taking FP_2-COOH as an example, the *in-situ* ATR-FTIR spectra of FP_2-COOH + CO_2 binary system were collected at 60.0 °C under an FP_2-COOH volume of 10.0 mL. The pressure was increased in steps of 1.0 MPa up to 8.0 MPa, of 0.5 MPa up to 10.0 MPa, of 0.2 MPa up to 12.0 MPa, of 1.0 MPa up to 20.0 MPa, and of 2.0 MPa up to 38.0 MPa (as shown in Fig. 2).

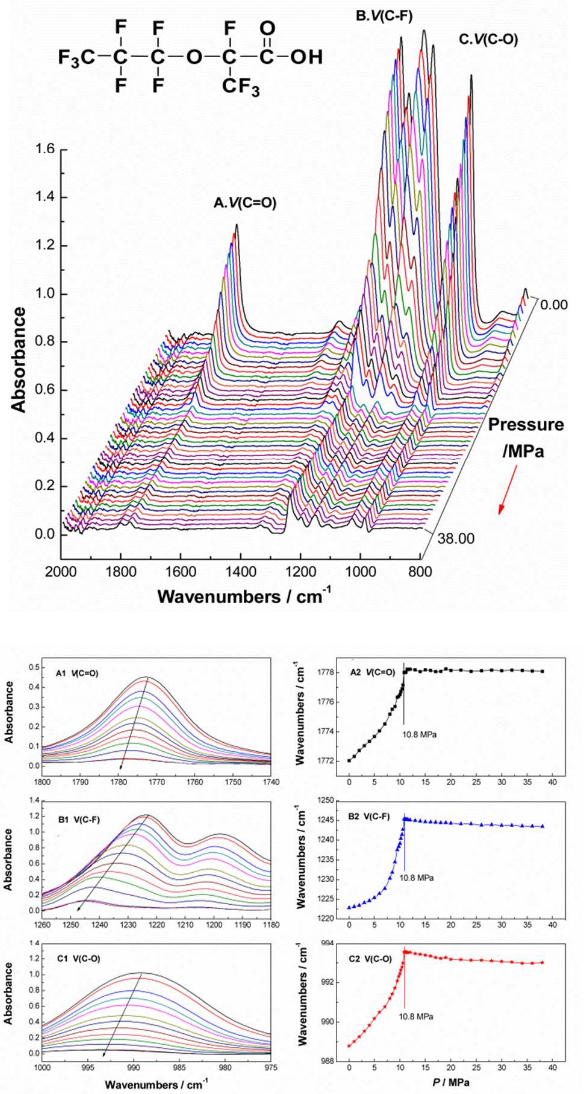


Fig. 2 *In-situ* ATR-FTIR spectra of the FP_2-COOH + CO_2 system under different pressures at 60.0 °C. The volume of FP_2-COOH used was 10.0 mL. The resolution of the ATR-FTIR was 2.0 cm^{-1}. The number of scans accumulated was 20. The arrows showed the spectra evolution versus the increase of pressure of the binary system.

As shown in Fig. 2, a dramatic blue-shift together with an obvious inflection point and a subsequent very slight red-shift are clearly observed in the evolution curve of the probed *v*(C=O), *v*(C-F) and *v*(C-O) in FP$_2$-COOH + CO$_2$ system. Though the probe bands blue-shift in different extent, the inflection point pressures in the vibrational absorption evolution curves of the probed functional groups are found to be exactly the same, namely 10.8 MPa. Similar vibrational absorption evolutions are also generally observed in the rest oligomer + CO$_2$ systems with considerably good reproducibility (as shown in Table S1 in Electronic Supplementary Information (ESI)). To the best of our knowledge, similar observation has not been reported by others. Very few literatures have involved the blue-shift in FTIR spectra of small molecules or polymers with scCO$_2$ as the pressure increased.[22]

We believe that such evolution of the vibrational absorption is directly rooted in and dynamically induced by the variation of the intermolecular interactions in the oligomer + CO$_2$ systems as the pressure and/or the temperature varied during the solvation process. The solvation mechanism of liquid monomers in gaseous and supercritical CO$_2$ together with the unusual vibrational absorption evolution has been primarily demonstrated by introducing the concepts of P_T, as well as the resultant interactions of σ(A-B) and σ(B-B) in our recent study,[10a] where P_T, namely transition pressure, is the inflection point pressure in the vibrational absorption evolution curve of the probed functional groups in the system investigated, and is assumed to be the lowest pressure at which the dispersate/solute could be miscible with CO$_2$ under isothermal conditions. Therefore, it is believed that a lower P_T means a better solubility of the corresponding dispersate/solute in CO$_2$, and possibly, stronger intermolecular interactions between the dispersate/solute and CO$_2$. Based on such cognition or understanding, the impacts derived from various factors on the solvation behaviors of the epoxide oligomers in CO$_2$ are systematically discussed.

Impacts on the solvation behaviors of epoxide oligomers in CO$_2$

Temperature. Three model epoxide oligomers, namely PEO400-Ac$_2$, PPO400-Ac$_2$ and FP$_3$-COOH were employed and the impacts of temperature on the solvation behaviors of the oligomers were investigated. The solvation and dispersion processes of the oligomers were *in-situ* monitored at temperature ranges of 40.0-70.0 °C. The absorption centers of probe bands (namely *v*(C=O) and *v*(C-O) in PEO400-Ac$_2$ and PPO400-Ac$_2$, *v*(C-O) and *v*(C-F) in FP$_3$-COOH) were extracted from the *in-situ* FTIR spectra, and plotted versus the pressure of the system to obtain the absorption evolutions of the absorption bands and detect the P_T of the oligomer + CO$_2$ systems, as shown in Fig. 3. The relationship between P_T and temperature in the systems is shown in Fig. 4.

As is clearly seen in Fig. 3(A), for PEO400-Ac$_2$ + CO$_2$ at a certain temperature, whichever probe band was investigated, the P_T obtained is found to be identical at the temperature as was expected. Similar results are also observed in the other two oligomer + CO$_2$ systems, as shown in Fig. 3(B) and (C), respectively. Moreover, it is observed that the P_T of every oligomer + CO$_2$ system investigated increases (almost linearly) with the increase of temperature but in different extent among the systems, as shown in Fig. 4.

It is clearly seen that as the temperature increases from 40.0 to 70.0 °C, P_T of PEO400-Ac$_2$ + CO$_2$ system increases from 24.2 to 35.4 MPa, i.e., an incredible increase of 11.2 MPa was observed in view of the fact that the temperature merely

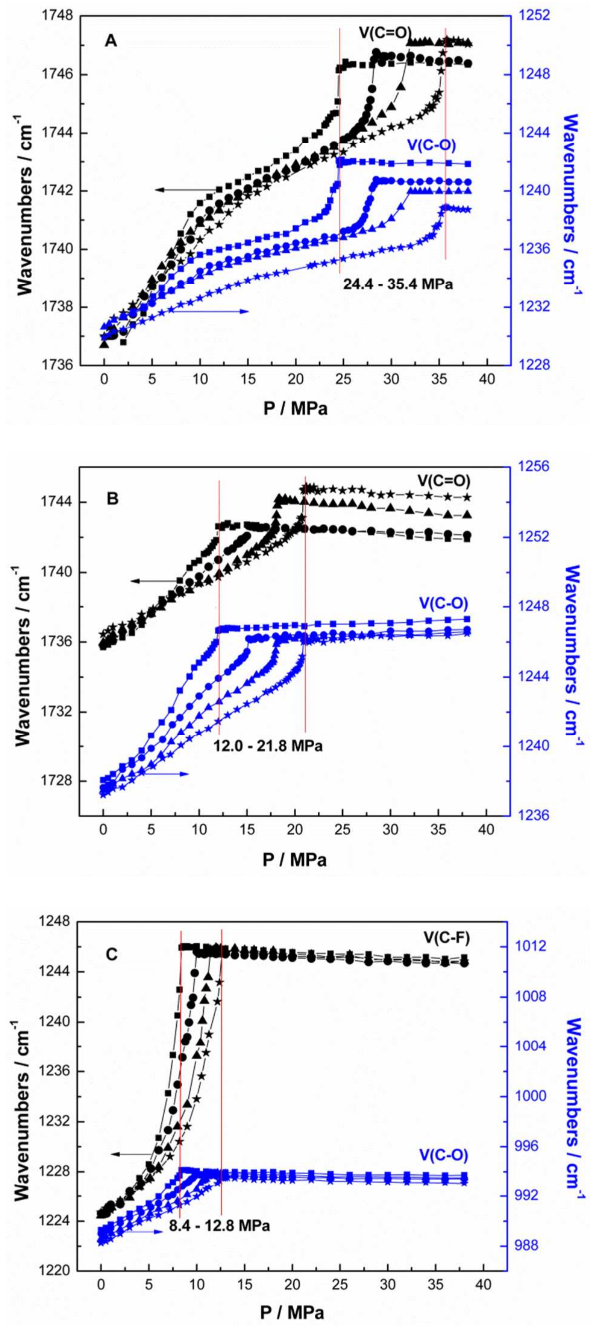


Fig. 3 Vibrational absorption eolution of the functional groups in the epoxide oligomer + CO_2 system at different temperatures (■ 40.0 °C; ● 50.0 °C; ▲ 60.0 °C; ★ 70.0 °C). (A) PEO400-Ac_2 + CO_2; (B) PPO400-Ac_2 + CO_2; (C) FP_3-COOH + CO_2. The volume of oligomer used was 10.0 mL. The resolution of the ATR-FTIR was 2.0 cm^{-1}. The number of scan accumulated was 20.

increased by 30 °C, as shown in Fig. 4. While as to the system of PPO400-Ac_2 + CO_2, P_T is found to increase from 12.0 to 20.7 MPa, increasing by 8.7 MPa in the same ranges of temperature. Interestingly, for FP_3-COOH + CO_2 binary system, P_T is found to only increase by 4.2 MPa (from 8.4 to 12.8 MPa). Clearly, temperature impacts distinctly on the P_T of the oligomer + CO_2 system, and thus plays a significant role in the solvation behaviors of the epoxide oligomers in CO_2. Possible reasons are presented as follows.

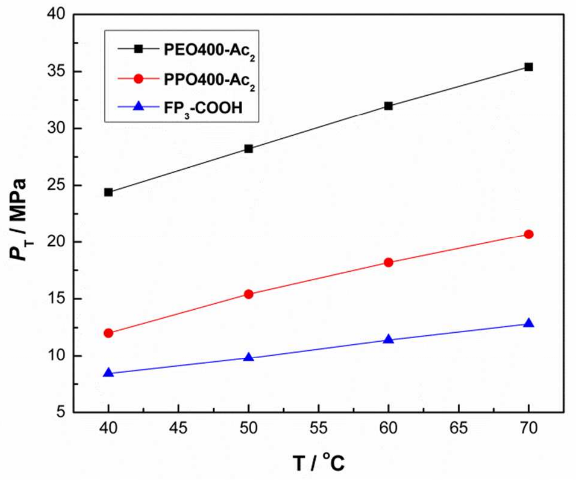


Fig. 4 Relationship between P_T and temperature in different epoxide oligomer + CO_2 systems.

It is known that the density as well as dielectric constant of CO_2 may decrease with the increase of temperature to a different extent. Based on our previous work,[10a] it is inferred that the solvability of CO_2 toward oligomer may decrease in step with the increase of temperature. Thus in order to offset the insufficient solvability of CO_2 resulted from the increase of temperature, the pressure must be further increased, which is believed to promote the increase of intermolecular interaction between CO_2 and the epoxide oligomers used, and help the self-interaction or cohesion among the molecules of the epoxide oligomers be balanced or even outweighed. Consequently, with the increase of temperature, the needed pressure where the epoxide oligomer is miscible with CO_2 becomes higher, i.e., the P_T of the corresponding system increases.

While it is found that both P_T (at the same temperature) and the increase extent of P_T (within the identical temperature ranges) differ distinctly among the model epoxide oligomer + CO_2 systems investigated (as shown in Fig. 4). We suggest that such observations directly root in the structural difference of the epoxide oligomer. Therefore, the impacts of such differences in the molecular weight, the end group and the repeated unit in the oligomers on the solvation behaviors of the oligomers in CO_2 were further excavated.

Molecular Weight. The solvation behaviors of three categories of epoxide oligomers (PEO-Ac_2, PPO-Ac_2 and FP_n-COOH) with a series of M_n in gaseous and supercritical CO_2 were investigated at 60.0 °C. The relationship between P_T of the oligomer + CO_2 system and M_n in every category of the oligomer is shown in Fig. 5.

As is shown in Fig. 5, it is clearly seen that in every category of epoxide oligomers studied, P_T of the oligomer + CO_2 systems is found to increase with the increase of M_n at the same temperature, but increase in severely different extents among the categories mentioned above. Moreover, it is surprisingly found that the P_T of every FP_n-COOH + CO_2 system is considerably moderate. While more importantly, the P_T varies quite gently with the M_n of FP_n-COOH. For example, as the M_n of FP_n-COOH increase from 164 to 4000, it is found that P_T of the FP_n-COOH +CO_2 systems increases from 9.8 to 16.3 MPa, i.e., a fairly slight increase of merely 6.5 MPa is incredibly observed in view of the prominent increase of the M_n of FP_n-COOH. While as to PPO-Ac_2 + CO_2 systems, with the increase of the M_n of PPO-Ac_2 from 280 to 1100, P_T is found to increase from 13.9 to 32.0 MPa. A distinct increase of 18.1 MPa of the P_T is obtained. However, for PEO-Ac_2 + CO_2 systems, P_T exhibits a severely sharp increase over 33.0 MPa, varying from 14.0 to more than 45.0 MPa, versus that the M_n of PEO-Ac_2 presents a slight increase from 146 to 718. Based on such observations, it is concluded that the M_n of the epoxide oligomers impacts significantly on the solvation behaviors in gaseous and supercritical CO_2.

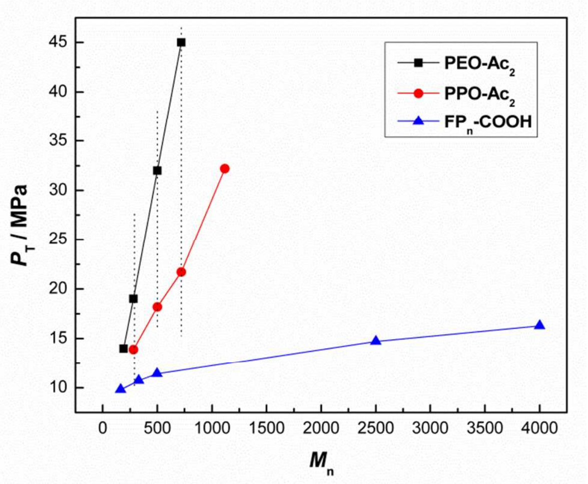


Fig. 5 Relationship between P_T and the M_n of different epoxide oligomer + CO_2 systems.

It is believed that the increase of molecular weight leads to the increase of the dispersion force,[10a,23] and further results in the increase of the self-interaction among the epoxide oligomer molecules, which impacts detrimentally on the solvation/dispersion of the epoxide oligomer in CO_2. While in order to offset or restrain such detrimental effect, higher CO_2 pressure is reasonably needed, since the increase of CO_2 pressure may contribute to enhancing the intermolecular interaction(s) between the epoxide oligomer and CO_2, and thus improve the solvability of CO_2 towards the epoxide oligomer. In view of the significant influence resulted from the M_n of the epoxide oligomers to the solvation of the oligomers in CO_2, it is indicated that the Van der Waals interaction, especially the dispersion force, may be the predominant contribution to the intermolecular interactions in the same category of epoxide oligomer + CO_2 system, and the solvation behaviors of the epoxide oligomers in CO_2, though other factor(s) may also play a role.[23,24]

End Group. The hydroxyl end group is believed to have distinctly negative impacts on the miscibility/solvability of oligomers/polymers in CO_2 due to the relatively strong hydrogen bonding among the dispersate molecules. Such impacts are even more so to that of the polyhydroxy compounds. This may mainly answer for the severely poor solubility of the carbohydrate and cellulose[25] in $scCO_2$. While it is reported that the solubility of poly(alkylene glycol)s in CO_2 can be obviously increased by endcapping one or both of the hydroxyl end group(s) through etherification.[18,24a] The impacts of the end group(s) on the solvation behaviors of the epoxide olimogers in CO_2 were explored in the present work.

As shown in Fig. 5, it is clearly seen that the P_T of PEO100-Ac_2+CO_2 system is merely 14.0 MPa at 60.0 °C, indicating that PEO100-Ac_2 possesses a considerably good miscibility/ solvability in $scCO_2$. However, as far as PEO100 is concerned, it is thoroughly another story. PEO100 (namely PEG100), a typical oligomer (dimer) of ethylene oxide with a molecular weight of 106 and with two hydroxyl groups connected to its chain ends, is observed cannot be miscible with CO_2 below 50 MPa at 60.0 °C. Similarly, due to the detrimental effects from the hydroxyl group were greatly restrained or thoroughly eliminated, the solubility of the corresponding esters is found to dramatically increase when the hydroxyl end groups in ethylene oxide oligomers with higher M_n were esterified (data not shown). The contribution of the introduced acetyl end group to the solvation behaviors of PEO-Ac_2/PPO-Ac_2 in CO_2 should be discerned and understood. So far carbonyl group, especially acetyl group, is accepted as a promising CO_2-philic group as it can facilitate some special interactions/attractions of carbonyl compounds with CO_2.[23,25,26] The LA-LB interaction between carbon atom of CO_2 and carbonyl O atom in the acetyl group endcapped epoxide oligomers, as well as the untraditional cooperative C-H···O hydrogen bonding between CO_2 and acetyl group of the epoxide oligomers, may significantly promote the solvation of the epoxide oligomers in $scCO_2$. Moreover, the favorable accessibility of carbonyl oxygen in the oligomers to CO_2 may also play a role. As a result, P_T of the corresponding epoxide oligomer + CO_2 binary system is found to be relatively low (as shown in Fig. 5). Clearly the end group impacts significantly on the solvation behaviors of the oligomers of ethylene oxide/propylene oxide in CO_2.

The impacts of carboxyl end group on the solvation behaviors of the carboxylic acid were also investigated. The P_T of FP_3-COOH + CO_2 system is obtained as 11.4 MPa. While after the carboxyl end group was endcapped *via* esterification with CH_3OH, the P_T of resulted FP_3-$COOCH_3$ + CO_2 system decreased to 10.7 MPa, i.e., a slight decrease of merely 0.7 MPa was achieved after the endcapping, as shown in Fig. 6 (in which the difference in the solvation behaviors of the 4 typical oligomers with a similar M_n of approximately is also illustrated). Clearly, though there does exist the intermolecular hydrogen bonding among FP_3-COOH, the P_T of FP_3-COOH + CO_2 is relatively low or at least quite moderate. It seems that the end group effect is not as remarkable as what was expected on the solvation behaviors of the oligomers of fluorinated epoxide in CO_2. Such results should be ascribed to the specific structure of repeated unit in the oligomers investigated, especially to the fluorinated group, and are further demonstrated as follows.

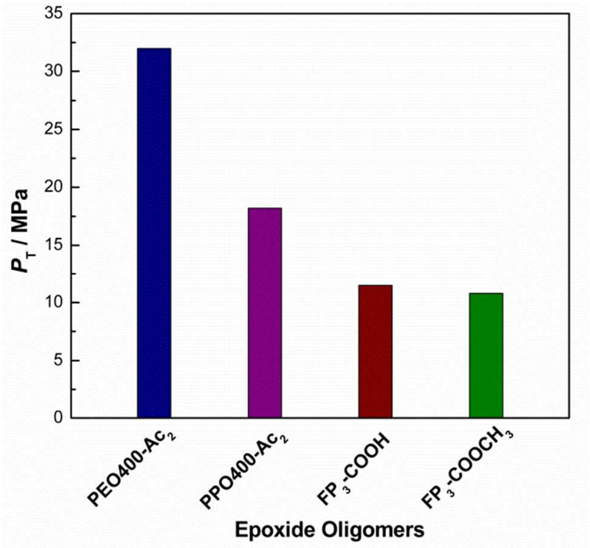


Fig. 6 P_T of the epoxide oligomer + CO_2 binary systems at 60.0 °C.

Structure of Repeated Unit

(1) *Branched Methyl Group**.*** The impacts from the branched methyl group on the solvation behaviors were investigated. It is clearly seen that the oligomers of PPO-Ac_2 disperse/dissolve much easier than PEO-Ac_2 in CO_2. The P_T of the PPO-Ac_2 + CO_2 systems is found much lower than that of PEO-Ac_2 + CO_2 systems at the same temperature under (almost) identical M_n of the oligomers, as shown in Fig.s 4 and 5. For example, PPO400-Ac_2 has an identical M_n (approximately 500) to that of PEO400-Ac_2. While the P_T of the systems of PPO400-Ac_2 + CO_2 and PPO400-Ac_2 + CO_2 at 60.0 °C is measured as 18.2 and 32.0 MPa, respectively. Since the key distinction between the two categories of dispersates is only that there is an additional branched methyl group attached to the repeated unit of PPO-Ac_2 (as shown in Scheme 1), the observed evident difference in the solvation behaviors must be rooted in such structural difference between the two dispersates.

We believe that the branched methyl group may benefit the solvation and dispersion of the PPO-Ac_2 and other derivatives from PPO in CO_2 to great extents. Compared with PEO-Ac_2, the branched methyl groups in PPO-Ac_2 increase the steric hindrance as well as the average distance between the oligomer/polymer chains (or at least the segments of the chains), thus may effectively weaken the cohesion and undermine the self-interaction(s) among the molecules of the dispersate. Moreover, the oxygen atoms in the repeated unit might be *freer* since the possibly related (possible) self interaction(s) is restrained or weakened to different extents. This may (at least partly) explicate or answer for the observed reduced crystallization propensity of poly(propylene glycols).[21] Consequently, the accessibility of the oxygen atoms in the repeated unit to CO_2 may be distinctly enhanced. The improved accessibility along with the *freer* oxygen atoms in the repeated unit in such epoxide oligomer facilitates the increase of the intermolecular attraction between the oligomer and CO_2, and results in a better solubility of the PPO-Ac_2 in CO_2, as well as much lower P_T of the PPO-Ac_2 + CO_2 systems. It is suggested that the LA-LB existed between the O atoms in the PPO-Ac_2 and the C atom in CO_2 might be (slightly) stronger than that in PEO-Ac_2 + CO_2 systems.

(2) *Fluorinated Group*. The fluorinated group is accepted as a kind of CO_2-philic group since numerous fluorinated organics exhibit prominent solubility in scCO_2. The affinity between the fluorinated group and CO_2 has been a common sense for years, while the nature of such affinity is still to be elucidated.[27] In order to evaluate the contribution of fluorinated group to the special CO_2-philicity of fluorinated oligomers/polymers, the solvation of fluorinated epoxide oligomers (FEO), namely FP_n-COOH in CO_2 was investigated. As is described above, the P_T of the FP_n-COOH + CO_2 systems is found to increase with the increase of the M_n and/or temperature as is expected. While even though there is a carboxyl group attached to the chain end of FP_n-COOH, which is believed to have detrimental effects on the miscibility of FP_n-COOH with CO_2, it is surprisingly that both the P_T of the FP_n-COOH + CO_2 systems and the variation extents of the P_T with temperature and/or M_n are found much lower than that of PPO-Ac_2 + CO_2 systems, as shown in Fig.s 4 and 5. For example, the P_T of FP_{24}-COOH + CO_2 system was obtained as merely 16.3 MPa at 60.0 ^{o}C in view of the molecular weight (M_n of approximately 4000) and prominently high concentration in scCO_2 (volume ratio of 20% or weight ratio of over 40%). Clearly, it is indicated that among the three categories of the epoxide oligomers investigated, the oligomers of hexafluoropropylene oxide (PHFPO) possess the best solubility/solubilization in scCO_2. Such enhanced solubility in scCO_2 should undoubtedly be attributed to the unique contribution from the the fluorinated groups.

As was preliminarily demonstrated in our previous work,[10a] the enhanced solubility of fluorinated oligomers/polymers in CO_2 could be mainly attributed to the special interaction between C-F and CO_2. We believe that the introduction of F atoms to the repeated unit of FP_n-COOH may increase the intermolecular attraction between the oligomer segments and CO_2. Moreover, similar to that of PPO-Ac_2, the branched trifluoromethyl groups may effectively improve the accessibility of the atoms (F and O) in the repeated unit of FP_n-COOH to CO_2. As is shown in Fig. 3(C), the maximum blue-shift of the *v*(C-F) in FP_2-COOH is found to be approximately 22 cm^{-1}, which is much higher than that of *v*(C-O). Such blue-shift is believed to be dynamically induced by the variation of the intermolecular interaction in the FP_3-COOH + CO_2 system, and similar shift was once employed to evaluate the enthalpy of association/interaction.[23,28] Since no exact measurement is evident from our present data, the rough estimation about the interaction enthalpy between FP_3-COOH and CO_2 is postulated as nearly 20 kJ·mol^{-1}. Such a surprisingly big value of interaction enthalpy might be the eagerly expected evidence for the existence of enhanced attraction between FP_3-COOH and CO_2. It is also inferred that among the interactions between C-F/C-O/C=O in FP_3-COOH and CO_2, the special interaction between C-F and CO_2 may contribute the most to the intermolecular interaction/attraction between the FP_3-COOH and CO_2. However, even though such intermolecular attraction(s) between the FP_n-COOH and CO_2 does play a significant role to a better solubility of FP_n-COOH in CO_2, we believe that the unique fluorine repulsion among FP_n-COOH oligomers should also be highly valued.

Owing to the biggest electronegativity of F atom along with the nearly shortest C-F covalent bond, there must be an additional electrostatic repulsion among (the fluorinated portion of) FP_n-COOH oligomers. Similar fluorine repulsion in poly(vinyl trifluoroester) has been reported by Destarac et al.[28] We suggest that such fluorine repulsion may distinctly undermine or decrease the self-interaction among FP_n-COOH oligomers, and may definitely improve the accessibility of the fluorinated repeated unit of FP_n-COOH to CO_2 to different extents.

Briefly, we believe that it is the synergistic effects of the increased intermolecular attraction between the FEO and CO_2, the decreased self-interaction resulted from the effectively fluorine repulsion among the oligomers themselves, and the specially favorable accessibility of the fluorinated repeated unit to CO_2 that predominantly answer for the enhanced/excellent solubility of FP_n-COOH in CO_2, as well as the lowest P_T in the three categories of epoxide oligomer + CO_2 model systems investigated. Based on all the observations mentioned above, it is strongly suggested that the FEO investigated may be the most soluble species in scCO_2 and thus may act as the ideal solubilizer or solubilizing chain after being transplanted or grafted into some targeted molecules. Further investigation concerning the special affinity of fluorinated organics to CO_2, especially the unique fluorine repulsion among a variety of fluorinated organics *via* both experimental way and simulation method is still going on.

Experimental section

Materials and apparatus

Oligomers of propylene oxide (PPO, Mn = 200, 400, 600, 1000), oligomers of ethylene oxide (PEO, Mn = 100, 200, 400, 600), acetyl chloride (CH_3COCl), dichloromethane (CH_2Cl_2), pyridine (C_5H_5N) and 4-dimethylaminopyridine (DMAP) are analytical purity and used as received. Oligomers of hexafluoropropylene oxide with a carboxylic group in one end (FP_n-COOH (n = 15 (M_n = 2500) and 24 (M_n = 4000)) were purchased from DuPont, used as received. Oligomers of hexafluoropropylene oxide with an acyl fluoride group in one end (FP_n-COF, n = 1, 2, 3) were intentionally prepared following the similar procedure in our previous work.[10a] Other chemicals employed in this research are all analytical purity, and used as received. Methanol (analytical purity) was refluxed under magnesium (Mg) followed by distilled before used. Carbon dioxide (CO_2, 99.999% purity) and nitrogen (N_2, 99.995% purity), were used as received.

HP ATR-FTIR experiments were performed by using a PerkinElmer Spectrum 400 FTIR/NIR spectrometer which was supported by Spectrum Software (V 6.3.5, PerkinElmer) for data acquisition and processing. The spectrometer was intentionally modified by replacing the standard sample accessories with a set of specially designed fiber sensor acting in attenuated total reflection (ATR) mode, similarly to that described in our previous work.[10a] Every ATR-FTIR spectrum was recorded over wavenumbers ranges of 4000-650 cm^{-1} with a resolution of 2 cm^{-1} under 20 scans.

Preparation and characterization of the model epoxide oligomers

The model oligomers of propylene oxide (PPO-Ac_2) and ethylene oxide (PEO-Ac_2) were prepared *via* the esterification of the corresponding oligomers of epoxide with two hydroxyl groups connected to the chain ends. The model oligomers of hexafluoropropylene oxide (FP_n-COOH, n=1, 2, 3) were prepared *via* the hydrolysis of corresponding oligomers of FP_n-COF. The model oligomer of FP_3-$COOCH_3$ was prepared *via* the esterification of FP_3-COF with methanol. The oligomers of the model epoxides synthesized were characterized with FTIR and NMR. The FTIR spectra were measured on a Bruker Tensor 27 FTIR Spectrophotometer in KBr disks. ^{1}H NMR and ^{13}C NMR spectra were determined on an AVANCE 400 superconducting Fourier digital NMR instrument (400 MHz for proton) at 25 ^{o}C.

***PEO-Ac$_2$* and *PPO-Ac$_2$*.** Typical experimental procedure for the preparation of PEO-Ac_2 or PPO-Ac_2 was illustrated by using the esterification of PEO400 with acetyl chloride, and described as follows. A three-neck round-bottomed flask, equipped with a dropping funnel and a reflux condenser, was charged with PEO400 (40.0 g, 0.1 mol), pyridine (15.8 g, 0.2 mol), DMAP (0.2 g, 1.6 mmol) and CH_2Cl_2 (70 mL). A solution of acetyl chloride (31.4 g, 0.4 mol) in CH_2Cl_2 (10 mL) was transferred into the dropping funnel and added dropwise to the flask in approximately 4 h under stirring at 0 ^{o}C. Then the mixture in the flask was heated to 50 ^{o}C and kept slightly boiling overnight. After the mixture was filtered, the filtrate was collected, washed (with an aqueous solution of $NaHCO_3$), dried and distilled under vacuum to obtain the desired product of PEO400-Ac_2 (a colorless viscous liquid with a yield of 90%). The FTIR and NMR spectra of PEO400-Ac_2 and PPO400-Ac_2 are shown in Fig.s S1 and S2 in ESI, respectively.

***FP$_3$-COOCH$_3$*.** *Caution: The reactor should be carefully dried. More importantly, the released poisonous gas (HF) during the reaction process should be carefully treated (absorbed).*
The model oligomer of FP_3-$COOCH_3$ was prepared *via* the esterification of FP_3-COF with methanol, following the similar procedure reported by Paleta et al.[20] The product of FP_3-$COOCH_3$ was characterized *via* FTIR and NMR. The spectral results are shown in Fig. S3 in ESI.

***FP$_n$-COOH* (n =1, 2, 3)**. The model oligomers of FP_n-COOH (n =1, 2, 3) were prepared *via* the hydrolysis of the corresponding FP_n-COF with the moisture in air at a room temperature. The hydrolysis process was *in-situ* monitored *via* an FTIR system. Taking the hydrolysis of FP_3-COF as an example, the obtained *in-situ* FTIR series of the hydrolysis system are shown in Fig. 1. Finally, the targeted FP_3-COOH, a colorless viscous liquid, was successfully obtained with a yield of approximately 99%.

Monitoring the solvation processes and phase behaviors of oligomer+CO_2 system

Caution: Proper precautions (including but not limited to the use of blast shields and pressure relief unit) should be taken in such high-pressure experiments so as to minimize or eliminate the potential risks of personal injury. The solvation processes of the model oligomers of epoxide in gaseous and supercritical CO_2 were probed using the HP ATR-FTIR following the similar procedure presented in our previous work.[10a] Taking FP_2-COOH as an example, a typical experimental procedure is described as follows.

After preheated to a certain temperature (mostly at 60.0 °C), the view cell of the HP ATR-FTIR was purged with N_2 so as to eliminate the residual moisture and CO_2 in the system until no detectable IR absorption of possible residuals could be observed in a baseline. Then 10.0 mL of FP_2-COOH was injected into the view cell via a special syringe through the inlet of the view cell prior to it was closed, followed by stirring with a PTFE-coated magnetic stir bar at a speed of 300 rpm. Subsequently, CO_2 was charged stepwise into the view cell to solvate and disperse the previous injected model oligomer of FP_2-COOH till the pressure was up to 40.0 MPa. Simultaneously, the *in-situ* FTIR spectral series of the FP_2-COOH + CO_2 system were collected at specified pressure intervals while stirring continued throughout the solvation process. The evolution of peak position of the vibrational bands was dynamically detected in step with the increase of pressure. Followed by the absorption band centers of ν(C-F), ν(C=O) and/or ν(C-O) were extracted from the initial *in-situ* FTIR spectra, respectively, and plotted versus the pressure of the system. In this way the absorption evolutions of the vibrational bands in FP_2-COOH + CO_2 system were sketched, and from which the corresponding transition pressure (P_T) of every binary system was measured (with errors within 0.1 MPa). During the solvation process, the phase behaviors of the FP_2-COOH + CO_2 system were directly and visually observed through the sapphire windows of the view cell.

Conclusions

Three categories of fourteen epoxide oligomers with different molecular weights were intentionally synthesized. The intermolecular interactions between the epoxide oligomers and CO_2 in gaseous and supercritical CO_2 were successfully evaluated using a set of high-pressure *in-situ* ATR FTIR monitoring system. Through the dynamically associating the subtle variations of the vibrational absorption of the functional groups with the detailed evolution of the intermolecular interaction(s) during the solvation processes, the intermolecular-interaction-dominated solvation behaviors of the oligomers in CO_2 were excavated and discerned. The key role of the intermolecular interactions on the enhanced solubility of FEO in $scCO_2$ was established and major factors impacting on the molecular interplay between the epoxide oligomers and CO_2 were systematically evaluated. Whereas there are still issues to be explored, the present research may be the first example that definitely discloses the fact that the FEO investigated possesses the uniquely enhanced solubility in $scCO_2$, which are suggested to be the most soluble species in $scCO_2$ in view of the specially favorable intermolecular interactions as well as the excellent accessibility of the repeated unit to CO_2 molecule. We firmly believe that after being transplanted or grafted into the targeted molecule, such FEO may act as the ideal solubilizing chain in developing a series of novel fluorinated monomers, ligands/complexes and surfactants applied in $scCO_2$ system. Moreover, the developed high-pressure *in-situ* ATR FTIR system is proved to be a promising technology to explore the intermolecular interactions in $scCO_2$. This research is expected to promote the polymerization, catalysis, extraction and other related researches/applications in $scCO_2$ systems.

Acknowledgements

The authors gratefully acknowledge the financial support from the 111 Project (B14041), the National Natural Science Foundation of China (21176151, 21306111, 21327011), the Program for Changjiang Scholars and Innovative Research Team in University (IRT_14R33), Natural Science Foundation of Shaanxi Province (2014JM2034), the Fundamental Research Funds for the Central Universities (GK201401001, GK201402050), and the Shaanxi Innovative Team of Key Science and Technology (2012KCT-21, 2013KCT-17).

Notes and references

1 (a)L. Y. Lu, M. L. Berkowitz, *J. Am. Chem. Soc.* 2004, **126**, 10254-10255; (b) E. Torino, E. Reverchon, K. P. Johnston, *J. Colloid Interface Sci*. 2010, **348**, 469-478.

2 (a) L. Y. Wang, L. H. Zhuo, C. Zhang, F. Y. Zhao, *Chem. Eur. J.* 2014, **20**, 4308-4315; (b) F. W. Li, Q. L. Suo, H. L. Hong, N. Zhu, Y. Q. Wang, L. L. Guo, L. M. Han, *J. Supercrit. Fluids* 2014, **92**, 70-74.

3 (a) M. H. Lee, H. Y. Lin, J. L. Thomasw, *J. Am. Ceram. Soc*. 2006, **89**, 3624-3630; (b) T. Hasell, C. D. Wood, R. Clowes, J. T. A. Jones, Y. Z. Khimyak, D. J. Adams, A. I. Cooper, *Chem. Mater*. 2010, **22**, 557-564.

4 A. M. B. Osuna, W. P. Chen, E. G. Hope, R. D. W. Kemmitt, D. R. Paige, A. M. Stuart, J. L. Xiao, L. J. Xu, *J. Chem. Soc. Dalton Trans*. 2000, **22**, 4052-4055.

5 (a) J. C. Meredith, K. P. Johnston, J. M. Seminario, S. G. Kazarian, C. A. Eckert, *J. Phys. Chem.* 1996, **100**, 10837-10848; (b) M. Saharay, S. Balasubramanian, *J. Phys. Chem. B* 2006, **110**, 3782-3790; (c) K. A. Consani, R. D. Smith, *J. Supercrit. Fluids* 1990, **3**, 51-65.

6 B. Tan, C. L. Bray, A. I. Cooper, *Macromolecules* 2009, **42**, 7945-7952.

7 (a) F. Chang, H. Kim, Y. Kwon, *J. Chem. Eng. Data* 2009, **54**, 1262-1265; (b) P. G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 1999, **99**, 475-493; (c) P. G. Jessop, *J. Supercrit. Fluids* 2006, **38**, 211-231; (d) N. Dahmen, P. Griesheimer, P. Makarczyk, S. Pitter, O. Walter, *Journal of Organometallic Chemistry* 2005, **690**, 1467-1473.

8 M. Saharay, S. Balasubramanian, *J. Phys. Chem. B* 2006, **110**, 3782-3790.

9 (a) W. Z. He, Q. L. Suo, H. L. Hong, G. M. Li, X. H. Zhao, C. P. Li, A, S. *Ind. Eng. Chem. Res.* 2006, **45**, 2108-2115; (b) X. Zhang, B. Han, Z. Hou, J. Zhang, Z. Liu, T. Jiang, J. He, Li H. *Chem. Eur. J.* 2002, **8**, 5107-5111; (c) I. Skarmoutsos, D. Dellis, J. Samios *J. Chem. Phys*. 2007, **126**, 224503.

10 (a) J. G. Chen, X. Liu, Z. W. Liu, D. D. Hu, C. J. Zhang, D. Xue, J. L. Xiao, Z. T. Liu, *Macromolecules* 2012, **45**, 4907-4919; (b) T. C asimiro, A. Shariati, C. J. Peters, M. N. Ponte, A. Aguiar-Ricardo, *Fluid Phase Equilibria* 2005, **228-229**, 367-371.

11 (a) A. V. Yazdi, E. J. Beckman, *Ind. Eng. Chem. Res.* 1996, **35,** 3644-3652; (b) J. M. DeSimone, Z. Guan, C. S. Elsbernd, *Science* 1992, **257**, 945-947; (c) L. Du, J. Y. Kelly, G. W. Roberts, J. M. DeSimone, *J. Supercrit. Fluids* 2009, **47** 447-457; (d) P. N. Bartlett,; D. C. Cook, M. W. George, J. Ke, W. Levason, G. Reid, W. Su; W. J. Zhang, *Phys. Chem. Chem. Phys*. 2010, **12**, 492-501.

12 (a) K. E. Laintz, J. J. Yu, C. M. Wai, *Anal. Chem*. 1992, **64**, 311-315; (b) K. E. Laintd, C. M. Wai, C. R. Yonker, R. D. Smith, *Anal. Chem*. 1992, **64**, 2875-2878.

13 Y. Lin, N. G. Smart, C. M. Wai, *Trends Anal. Chem.* 1995, **14**, 123-132.

14 S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem. Int. Ed. Engl.* 1997, **36**, 1628-1630.

15 (a) D. J. Adams, W. P. Chen, E. G. Hope, S. Lange, A. M. Stuart, A. West, J. L. Xiao, *Green Chemistry* 2003, **5**, 118-122; (b) S. Fujita, S. Fujisawa, B. M. Bhanage, Y. Ikushima, M. Arai, *Eur. J. Org. Chem*. 2004, **13**, 2881-2887; (c) F. Zhao, Y. Ikushima, M. Chatterjee, O. Sato, M. Arai, *J. Supercrit. Fluids* 2003, **27**, 65-72; (d) S. Fujita, S. Fujisawa, B. M. Bhanage, M. Arai *Tetrahedron Lett*. 2004, **45**, 1307-1310; (e) A. C. J. Koeken, M. C. A. van Vliet, L. J. P. van den Broeke, B. J. Deelman, J. T. F. Keurentjes, *Adv. Synth. Catal*. 2006, **348**, 1553-1559; (f) A. C. J. Koeken, M. C. A. van Vliet, L. J. P. van den Broeke, B. J. Deelman, J. T. F. Keurentjes, *Adv. Synth. Catal*. 2008, **350**, 179-188; (g) Y. Shimoyama, M. Sonoda, K. Miyazaki, H. Higashi, Y. Iwai, Y. Arai, *J. Supercri. Fluids* 2008, **44**, 266-272.

16 I. Kani, F. Sisman, *Journal of Molecular Catalysis A: Chemical* 2006, **259**, 142-149.

17 (a) D. A. Jackson, S. A. Mabury, *Environ. Sci. Technol*. 2013, **47**, 382-389;. (b) N. V. Ignat'ev, J. Bader, K. Koppe, B. Hoge, H. Willner *Journal of Fluorine Chemistry* 2015, **171**, 36-45.

18 C. Drohmann, E. J. Beckman, *J. Supercri. Fluids* 2002, **22,** 103-110.

19 S. V. Kostjuk, E. Ortega, F. Ganachaud, B. Améduri, B. Boutevin, *Macromolecules* 2009, **42**, 612-619.

20 O. Paleta, J. Paleček, J. Michálek, *Journal of Fluorine Chemistry* 2002, **114**, 51-53.

21 P. Lalanne, T. Tassaing, Y. Danten, F. Cansell, S. C. Tucker, M. Besnard, *J. Phys. Chem. A* 2004, **108**, 2617-2624.

22 (a) F. M. Fowkes, D. O. Tischler, J. A. Wolfe, L. A. Lannigan, C. M. Ademu-John, M. J. Halliwell, *J. Polym. Sci. Part A: Polym. Chem.* 1984, **22**, 547-566; (b) S. G. Kazarian, M. F. Vincent, F. V. Bright, C. L. Liotta, C. A. Eckert, *J. Am. Chem. Soc.* 1996, **118**, 1729-1736; (c) S. P. Nalawade, F. Picchiono, J. H. Marsman, L. P. B. M. Janssen, *J. Supercrit. Fluids* 2006, **36**, 236-244; (d) J. Andanson, F. Jutz, A. Baiker, *J. Phys. Chem. B* 2009, **113**, 10249-10254.

23 P. Raveendran, S. L. Wallen, *J. Am. Chem. Soc*. 2002, **124**, 12590-12599.

24 (a) B. Tan, C. L. Bray, A. I. Cooper, *Macromolecules* 2009, **42**, 7945-7952; (b) C. D. Wick, J. I. Siepmann, D. N. Theodorou, *J. Am. Chem. Soc.* 2005, **127**, 12338-12342.

25 (a) D. J. Heldebrant,; P. G. Jessop, *J. Am. Chem. Soc.* 2003, **125**, 5600-5601; (b) P. Raveendran, Y. Ikushima, S. L. Wallen, *Acc. Chem. Res.* 2005, **38**, 478-485.

26 (a) P. Raveendran, S. L. Wallen, *J. Am. Chem. Soc*. 2002, **124**, 12590-12599; (b) P. Raveendran, S. L. Wallen, *J. Am. Chem. Soc*. 2002, **124**, 7274-7275.

27 T. Seki, J. D. Grunwaldt, A. Baiker, *J. Phys. Chem. B* 2009, **113**, 114-122.

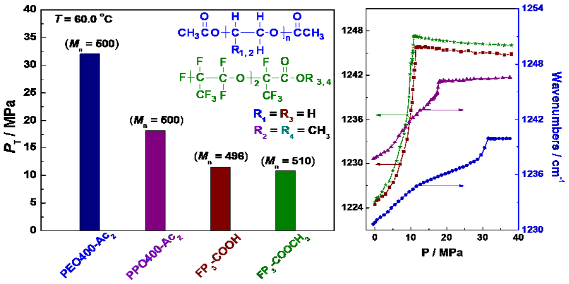
E. Girard, T. Tassaing, S. Camy, J. Condoret,; J. Marty, M. Destarac, *J. Am. Chem. Soc.* 2012, **134**, 11920-11923.

For Table of Contents Use only

Insight into the Role of Intermolecular Interactions on the Enhanced Solubility of Fluorinated Epoxide Oligomer in Supercritical CO_2

Gai-Gai Zhou, Jian-Gang Chen[*]*, Ming-Xi Wang, Min Zhang, Jing-Long Guo, Shukun Shen,*

Zhao-Tie Liu, Zhong-Wen Liu, Jinqiang Jiang, Jian Lu[*]



The key role of the intermolecular interactions on the enhanced solubility of fluorinated epoxide oligomer in $scCO_2$ was systematically discerned.