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Communication

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Enhancement of Poly(vinyl ester) Solubility in Supercritical CO_2 by Partial Fluorination: The Key Role of Polymer–Polymer Interactions

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Supporting Information

ABSTRACT: An enhancement of poly(vinyl ester) solubility in supercritical carbon dioxide (sc-CO_2) can be achieved by decreasing the strength of the polymer–polymer interactions. To demonstrate this, a library of statistical copolymers of vinyl acetate and vinyl trifluoroacetate was synthesized by RAFT/MADIX polymerization with varying compositions at a given number-average molecular weight. These copolymers exhibited unprecedentedly low cloud-point pressures in sc-CO_2 at 40 °C compared with previously reported poly(vinyl esters). Surface tension measurements combined with a computational approach evidenced the prominent role played by polymer–polymer interactions.

In the development of green chemistry solutions, the replacement of conventional organic solvents by "greener" ones has been identified as a key criterion to address the environmental challenges imposed by chemical synthesis, processing, and separations.[1] From this perspective, supercritical fluids represent a promising alternative because of their pressure- and temperature-tunable properties. In particular, supercritical carbon dioxide (sc-CO_2) has been considered a solvent with high potential to reduce environmental damage because of its low inflammability, cost, toxicity, reactivity, and critical temperature and pressure (31.1 °C, 73 bar). Surprisingly, academic research in the area of green solvents to date has somehow neglected carbon dioxide in favor of ionic liquids.[2] A reason for this relative detachment might be the feeble solvating power of sc-CO_2, which results in the low solubility or insolubility of a large variety of reactants, catalysts, and macromolecules. Indeed, sc-CO_2 is a nonpolar aprotic solvent with low polarizability, dielectric constant, and cohesive energy density, making it a poor medium to solubilize ionic or polar compounds. In particular, most commodity polymers possess limited solubilities in sc-CO_2 under mild conditions ($P < 350$ bar, $T < 100$ °C).[3,4] The only examples of highly CO_2-soluble polymers include high-molecular-weight (i.e., >10000 g·mol^{-1}) fluorinated polyacrylates,[5−7] perfluoroalkyl ethers,[8,9] and polysiloxanes.[4,10] In view of the aforementioned polymers, the solubility of polymers in sc-CO_2 was suggested to be mainly driven by weak polymer–polymer interactions (related to a low cohesive energy density) and a high entropy of mixing [related to a low glass transition temperature (T_g)].[4,11]

To a lesser extent, poly(vinyl esters) are another promising family of CO_2-philic polymers that present practical advantages of favorable price and toxicology compared with the habitual fluorinated and polysiloxane CO_2-philic polymers. Thus, a 5 wt % loading of a low-molecular-weight poly(vinyl acetate) (PVAc) [number-average molecular weight (M_n) = 2060 g·mol^{-1}] dissolves in CO_2 at 374 bar and 25 °C.[12] However, a chain-length dependence of the cloud-point pressure (P_{cloud})[12] and solubility[13] was also evidenced, which strongly limits the solubility of higher-molecular-weight PVAc. This solubility could be primarily explained by polymer–solvent interactions. Indeed, a specific Lewis acid–Lewis base (LA–LB) interaction between the electron-rich carbonyl functionality of the acetate group and the electron-deficient carbon atom of the CO_2 molecule that may explain their relatively high solubility was identified by IR spectroscopy.[14] The strength of this interaction was calculated to have a magnitude of half an interaction in a water dimer.[15] A cooperative C–H···O hydrogen bond between the acetate group and the CO_2 molecule was additionally revealed by ab initio calculations.[16] Nevertheless, stronger interactions between PVAc chains as well as a lower entropy of mixing may explain their lower solubilities in sc-CO_2 relative to fluorinated polyacrylates and polysiloxanes.

To overcome these intrinsic limitations, the design of PVAc-based copolymers with enhanced solubilities in sc-CO_2 was accomplished through the proper choice of a comonomer. As previously stated,[17,18] this comonomer should provide a decrease in the strength of the polymer–polymer interactions and/or higher entropic contributions deriving from enhanced entropy of mixing or free volume. This entropic approach has been recently studied through the introduction of a bulky comonomer. Vinyl acetate (VAc) was thus copolymerized with vinyl butyrate,[19,20] dibutyl maleate (DBM),[21] vinyl pivalate (VPi),[22] and vinyl octanoate[20] to promote the "CO_2-philicity" of these polymers in binary or ternary mixtures. The higher observed solubility was attributed to a higher free volume. However, the first strategy concerning polymer–polymer

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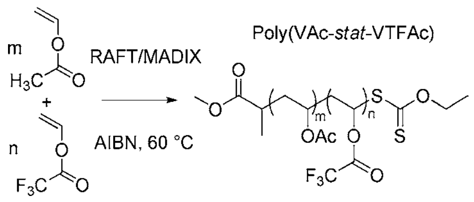
interactions has not been studied to date in the case of all-(vinyl ester)-based copolymers. Two criteria can be suggested to tailor these interactions through the copolymerization of VAc with a fluorinated comonomer. This comonomer, once copolymerized, should ideally present a low affinity for VAc units and a closely related steric hindrance to keep entropic effects at a minimum. Baradie and Shoichet fulfilled these criteria by synthesizing copolymers of VAc with various fluoroolefins such as tetrafluoroethylene in sc-CO_2, although no details on the polymer solubilities were given.[23] Alternatively, in this communication, a fluorinated analogue of VAc, namely, vinyl trifluoroacetate (VTFAc), was considered in order to probe the role of such interactions in the solubility of PVAc-based polymers in sc-CO_2. This comonomer was introduced into statistical copolymers with VAc in varying amounts with a constant M_n (targeted at 4000 g·mol^{-1}) (Scheme 1), and the solubility properties of the resulting copolymers were investigated by cloud-point measurements (with a polymer concentration equal to 0.2 wt %). Both the targeted M_n and polymer concentration were chosen to allow direct comparison of our results with the literature.[19]

Scheme 1. Synthetic Procedure for the Vinyl Ester Statistical Copolymers



The synthesis of well-defined copolymers primarily relies on the progress and perspectives opened by reversible-deactivation radical polymerization techniques (usually called controlled radical polymerization), which provide control of the growth of polymer chains in terms of molecular weights, microstructure, and dispersities. In the specific case of vinyl esters, reversible addition fragmentation chain-transfer (RAFT)[24]/macromolecular design via the interchange of xanthates (MADIX)[25] polymerization is undoubtedly the most convenient technique for producing well-defined poly(vinyl esters) through the introduction of a xanthate chain-transfer agent.[25,26] Thus, the polymerization of VTFAc was effectively mediated by an *O*-ethyl-*S*-(1-methoxycarbonyl)ethyl dithiocarbonate chain-transfer agent (Table 1, runs 1–3). Poly(vinyl trifluoroacetate) (PVTFAc) synthesized by RAFT/MADIX polymerization exhibited experimental M_n values close to their theoretical ones, as confirmed by ^{1}H NMR spectroscopy [Figure S2 and Table S1 in the Supporting Information (SI)]. The control of the polymerization of VTFAc was also confirmed by size-exclusion chromatography (SEC), which revealed that the M_n of the obtained polymers was inversely proportional to the xanthate concentration (runs 2 and 3; also see Figure S1). These polymers exhibited much lower dispersities ($Đ \approx 1.07$–1.11) compared with their counterparts synthesized by conventional radical polymerization (runs 1–3). Building on these results, we synthesized a library of PVTFAc-based copolymers with increasing VAc composition, targeting an M_n of 4000 g·mol^{-1} (Table 1, runs 4–9). The control was evidenced by the excellent matching between the theoretical M_n from NMR analysis and the experimental M_n obtained by SEC. The dispersity increased with increasing VAc content (up to $Đ \approx 1.31$ for the PVAc homopolymer), which may be related to a greater contribution of irreversible transfer to monomer and polymer[27] and/or head-to-head adducts[28] occurring during the course of the polymerization.

The solubility of these polymers in sc-CO_2 was then studied by cloud-point measurements. Briefly, a small amount of polymer (0.2 wt %) was introduced into a variable-volume cell filled with sc-CO_2. The pressure-induced isothermal (40 °C) monophasic-to-biphasic transition was then visually observed. Hence, the cloud point of a reference sample of PVAc (Table 1, run 9) was thus located at a pressure of 281 bar. With gradual incorporation of 11, 27, and 50 mol % VTFAc units into the polymer chains (runs 6–8), P_{cloud} dramatically decreased to 245, 212, and 177 bar (Figure 1). Thereafter, samples incorporating higher fractions of VTFAc (runs 4 and 5) exhibited a peculiar solubility behavior: a cloud-point-type transition could actually be observed at 203 and 271 bar in coexistence with a precipitated solid. For comparison, two samples of PVAc-based polymers incorporating bulky DBM or VPi comonomers were synthesized and evaluated as CO_2-philic materials (runs 10 and 11). Their P_{cloud} values were 269 and

Table 1. Experimental Results for the Synthesis, Solubility, and Physical Properties of the Vinyl Ester Statistical Copolymers[a]

		M_n (g·mol^{-1})							
run	sample	theor[b]	exptl[c]	$Đ$[c]	T_g (°C)	T_m (°C)	P_{cloud} (bar)[f]	θ (deg)[i]	γ (mN·m^{-1})[j]
1	PVTFAc	–	14300[d]	1.61[d]	55	148	n.d.[g]	–	–
2	PVTFAc	2200	4100[d]	1.07[d]	43	132	n.d.[g]	–	–
3	PVTFAc	4000	5900[d]	1.11[d]	43	137	n.d.[g]	88	30
4	PVAc$_{26}$-*stat*-PVTFAc$_{74}$	4200	4600	1.07	43	104	271[h]	89	30
5	PVAc$_{34}$-*stat*-PVTFAc$_{66}$	4200	3800[e]	1.04[e]	44	82	203[h]	88	30
6	PVAc$_{50}$-*stat*-PVTFAc$_{50}$	4200	4400	1.12	35	–	177	85	33
7	PVAc$_{73}$-*stat*-PVTFAc$_{27}$	4100	4400	1.16	30	–	212	76	38
8	PVAc$_{89}$-*stat*-PVTFAc$_{11}$	4300	4500	1.24	30	–	245	75	39
9	PVAc	4300	4200	1.31	21	–	281	58	49
10	PVAc$_{51}$-*alt*-PDBM$_{49}$	4400	3600	1.21	−12	–	269	80	36
11	PVAc$_{10}$-*stat*-PVPi$_{90}$	4300	4800	1.22	33	–	220	89	30

[a] See the SI for experimental details. [b] Determined by ^{1}H NMR analysis. [c] Determined by SEC in tetrahydrofuran (THF) with polystyrene standards. [d] Determined by SEC in *N*,*N*-dimethylformamide + 10 mM LiBr with poly(methyl methacrylate) standards. [e] Nearly isorefractive in THF. [f] Cloud-point pressures determined from the onset of turbidity with 0.2 wt % polymer in sc-CO_2 at 40 °C (standard deviation ± 3 bar, repeatability ±5 bar). [g] n.d. = not determined. [h] Determined from a biphasic mixture. [i] Contact angles, reported as average values of four measurements. [j] Surface tensions.

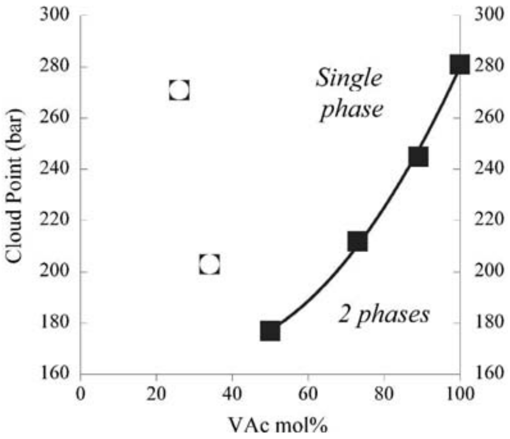


Figure 1. Cloud-point pressures of PVAc-*stat*-PVTFAc) (0.2 wt % polymer at 40 °C) as a function of VAc mole percent. Closed symbols denote a single cloud point, whereas open ones indicate the coexistence of a precipitate.

220 bar, respectively, highlighting the unprecedented pressure transition induced by the presence of VTFAc monomer units in a poly(vinyl ester) polymer chain. However, those pressures are anticipated to increase with either higher polymer molecular weights or polymer content.[29]

To gain an understanding of the observed solubility behavior, the respective contributions of polymer–solvent and polymer–polymer interactions were evaluated. Polymer–solvent interactions were calculated using model structures, namely, ethyl acetate (EtAc) and ethyl trifluoroacetate (EtTFAc), which are representative of the main functional groups of the backbone of PVAc and PVTFAc, respectively. The equilibrium geometries of these model structures and their complexes with CO_2 were optimized using density functional theory (DFT) at the CAM-B3LYP level with Dunning's aug-cc-pVDZ basis set (Figure 2).

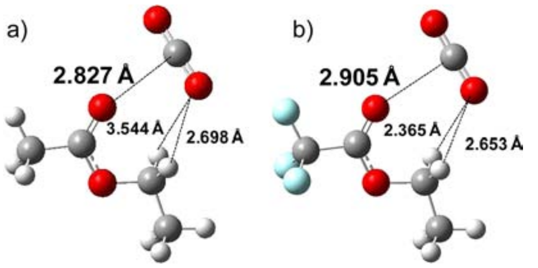


Figure 2. Optimized structures (CAM-B3LYP/aug-cc-pVDZ) for the ethyl side of the configuration of the (a) EtAc–CO_2 and (b) EtTFAc–CO_2 complexes.

This new functional was used because it provides a better account of dispersion forces than standard DFT methods.[30] The methyl side and trifluoromethyl side of the model compound–CO_2 complexes were not compared. Indeed, the fluorine atoms in EtTFAc were calculated to carry negative partial charges close to $-0.52e$, which render unfavorable any fluorine–CO_2 interactions.[31] The resultant equilibrium geometries on the ethyl side (shown in Figure 2) were equivalent for the two complexes, as CO_2 was found to be above the acetate group, where the oxygen atom interacts with CO_2 through an LA–LB interaction. A weak hydrogen bond appeared in both complexes between a hydrogen atom of the ethyl group and an oxygen atom of CO_2 (Figure 2). Such a structure is consistent with previous results obtained for methyl acetate complexes.[16] The intermolecular distances between the carbon atom of CO_2 and the oxygen atom of the acetate group ($d_{C\cdots O}$) were estimated as 2.827 Å for EtAc and 2.905 Å for EtTFAc. By the same token, the stabilization energy was significantly lower (0.5 $kcal \cdot mol^{-1}$) for the EtTFAc–CO_2 complex than for the EtAc–CO_2 complex. The interactions between CO_2 and the fluorinated moiety were consequently weaker. Additionally, steric effects could not account for this energy difference, given the geometry of the complexes. This was also supported by the charge distributions on the two model compounds (Table 2). The absolute partial charge on the oxygen atom of the carbonyl group was higher for EtAc than for EtTFAc. This might be related to the difference in the inductive effects imposed by the CH_3 and CF_3 groups. As a result, replacing the CH_3 group by a CF_3 substituent in the acetate functionality leads to a decrease in the partial negative charge on the carbonyl group that in turn leads to a decrease in the strength of the interaction between CO_2 and the acetate group. The solubility behavior of the PVAc-*stat*-PVTFAc copolymers was not consequently governed by polymer–solvent interactions.

Table 2. Basis-Set Superposition Error- and Zero-Point Energy-Corrected Interaction Energies (ΔE_{cor}), Intermolecular C···O Distances in the Acetate–CO_2 Complexes ($d_{C\cdots O}$), and Charges on the Oxygen Atom of the Isolated Acetate Molecule (q_O)

complex	ΔE_{cor} ($kcal \cdot mol^{-1}$)	$d_{C\cdots O}$ (Å)	q_O (e)
EtAc–CO_2	−1.92	2.827	−0.75
EtTFAc–CO_2	−1.44	2.905	−0.67

Polymer–polymer interactions were qualitatively estimated from surface tension (γ) values, which are commonly measured with sessile drop experiments. The water contact angle (θ) increased from 58° for a pure PVAc sample to 75, 76, 86, and 88° for PVAc-*stat*-PVTFAc copolymers with 11, 27, 50, and 66 mol % VTFAc, respectively (Table 1). From the empirical formula proposed by Li and Neumann,[32] γ values could be then extrapolated, and they dropped from 49 $mN \cdot m^{-1}$ for pure PVAc to 30 $mN \cdot m^{-1}$ at 66 mol % VTFAc. This corresponds to the surface tension of a 4 $kg \cdot mol^{-1}$ PVTFAc homopolymer (run 3). Interestingly, γ followed the same trend as the solubility (Figure S4). This clearly indicates the prominent role of polymer–polymer interactions in the solubility of amorphous PVAc-*stat*-PVTFAc polymers in sc-CO_2 and further confirms previous work where polymer–polymer interactions were postulated to be the key driving force in the solubility of polymers in sc-CO_2.[4,33] Therefore, the observed hybrid behavior with both a cloud point and an insoluble fraction (runs 4 and 5) may be explained by stronger polymer–polymer self-interactions resulting from the appearance of crystalline domains. To confirm this, additional measurements on the $PVAc_{34}$-*stat*-$PVTFAc_{66}$ sample (run 5) were performed at a higher temperature to melt the crystalline zones. As a benefit of the plasticizing effect of CO_2, a single cloud point was observed at 240 bar and 60 °C. As expected, this increase in solubility pressure corresponded with the decrease in sc-CO_2 density at higher temperatures. In light of this, stronger polymer–polymer interactions could explain the lower solubility observed for the $PVAc_{51}$-*alt*-$PDBM_{49}$ sample (run 10), although its lower T_g should favor its mixing entropy. On the other hand, the PVAc-

stat-PVPi sample (run 11) exhibited a γ value equivalent to that for the $PVAc_{34}$-*stat*-$PVTFAc_{66}$ sample even though P_{cloud} was nearly 50 bar higher. This may suggest that interactions between VAc and VPi units are more enthalpically favorable than those between VAc and VTFAc ones, thus decreasing the CO_2 solubility.[18]

In conclusion, PVAc has usually been regarded as a CO_2-philic polymer, mainly focusing on its specific LA–LB and hydrogen-bond-type polymer–solvent interactions. Here, the incorporation of a fluorinated monomer, VTFAc, in PVAc-based polymers dramatically increased their solubility properties. Both computational modeling and surface tension measurements demonstrated that decreasing the strength of the polymer–polymer interactions is the best lever to enhance the solubility of poly(vinyl ester) copolymers in sc-CO_2, while entropic factors play only a secondary role. This work consequently sheds new light on the "CO_2-philicity" of polymer materials and poly(vinyl esters) in particular. This should help the challenging design of highly CO_2-soluble polymer materials[13,34] and amplify their use as stabilizers in dispersion polymerizations[19,20] or as polymer templates in the synthesis of porous organic materials.[35]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and supplementary results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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