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Copolymerization of Tetrafluoroethylene and 2,2-Bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole in Supercritical Carbon Dioxide

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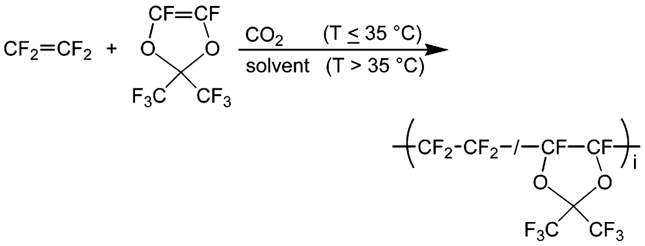
ABSTRACT: Copolymers of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) were synthesized in carbon dioxide at low temperatures. Bis(perfluoro-2-*N*-propoxypropionyl) peroxide was used as initiator. A range of copolymers with various compositions and different molecular weights were prepared in yields as high as 74%. The glass transition temperature of the copolymers increased with increasing PDD content and ranged from 67 to 334 °C for the PDD homopolymer. The phase behavior was found to depend on the feed composition. A comparison of a fully fluorinated commercially available product with a sample synthesized in carbon dioxide (without post-fluorination procedures) to match the composition and the molecular weight of the commercial sample showed no significant difference using IR spectroscopy, NMR spectroscopy, and differential scanning calorimetry, indicating similar microstructures. A simple method to determine the copolymer composition based on infrared spectroscopy was developed.

Introduction

Teflon AF is an amorphous copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD) (Scheme 1). It combines the properties of amorphous plastics like good optical transparency and solubility in organic solvents with those of perfluorinated polymers like high thermal stability, excellent chemical stability, and a low surface energy. Moreover, Teflon AF has some unique properties: it has the lowest dielectric constant (1.90 for Teflon AF 2400) and the lowest refractive index (1.29 for Teflon AF 2400) known for a solid organic polymer.[1] The low refractive index and exceptional optical clarity from ultraviolet into infrared wavelengths makes it well-suited for use as an optical material. Because of its low dielectric constant, it is also considered for use as a dielectric material for high-density integrated circuits.[2]

Scheme 1. Structure of Teflon AF



Carbon dioxide has been shown to plasticize many polymers[3] and even dissolve amorphous fluorinated polymers at accessible pressures and temperatures. It has also been demonstrated to be an excellent reaction medium for a number of polymerizations.[4−12] Using CO_2 as reaction medium has several advantages compared to conventional techniques. First, it is nontoxic and inexpensive especially compared to solution polymerization where fluorinated solvents have to be used. Second, the polymer can be synthesized and easily isolated in a dry and pure form. No additional workup is necessary to remove the solvent or water which eliminates the need for wastewater treatment. Many properties of CO_2, such as density, are said to be tunable, meaning that small changes in pressure or temperature lead to significant changes. The tunability of CO_2 can affect the solvancy of the medium and therefore impact phase equilibria and partition coefficients in heterogeneous systems. Free radical initiators have high efficiencies and acceptable decomposition kinetics[13] in CO_2 and do not exhibit appreciable chain transfer. Moreover, TFE is made safe to handle by forming a mixture of TFE and CO_2 which is nonignitable.[14] Nevertheless, precautions should be taken when handling TFE. TFE can decompose explosively under pressure and temperatures above −20 °C even in the absence of oxygen to form carbon and tetrafluoromethane. At low temperatures in the presence of oxygen, TFE can form dangerous peroxides. In the presence of oxygen at elevated temperatures, TFE burns, giving tetrafluoromethane and CO_2. In this paper a new method for the synthesis of TFE/PDD copolymers in carbon dioxide at low reaction temperatures is presented.

Experimental Section

Reagents. TFE was obtained from DuPont as a 50 wt % mixture in CO_2 and used as received. PDD (DuPont) was purified by filtration through a column filled with silica gel (230−400 mesh, Sigma). The column was cooled with dry ice because PDD has a low boiling point (33 °C). Teflon AF 1601 (fluorinated and unfluorinated) was obtained from DuPont. SFC purity CO_2 was obtained from Air Products. Perfluoro-2-hexyltetrahydrofuran (Fluorinert FC-75 produced by 3M) was used as received. Bis(perfluoro-2-*N*-propoxypropionyl) peroxide was prepared in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), according to a published procedure,[15] and stored

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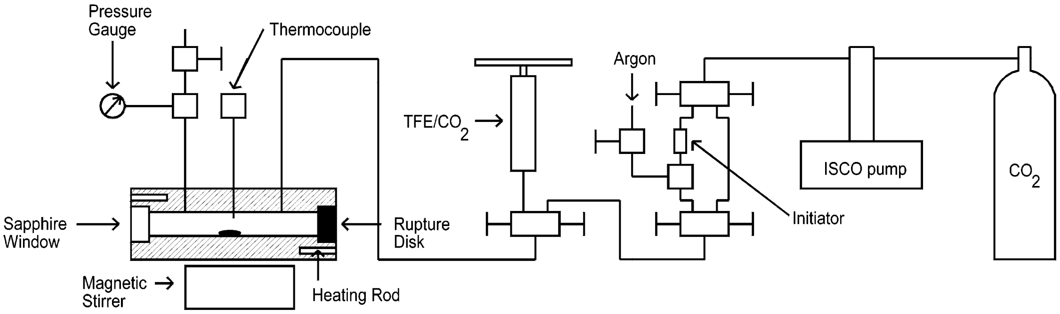


Figure 1. Schematic of the experimental setup.

Table 1. Reaction Conditions and Properties of TFE/PDD Copolymers (p = 2000 psi (138 bar), t = 5 h, T = 35 °C)

			PDD in polymer						
no.	T (°C)	PDD in feed (mol %)	NMR (mol %/wt %)	IR (mol %)	c^a (%)	amount initiator^b (mol %)	yield (%)	intrinsic viscosity (mL/g)	$T_g{}^d$ (°C)
1	35	20	*e*		18	0.1	66		67
2	35	30	29.7/50.8	30.2	20	0.1	51		76
3	35	40	40.5/62.4	41.2	19	0.1	59		92
4	35	50	48.0/69.3	48.4	24	0.1	34	80	109
5	35	50	51.8/72.4	52.2	21	0.3	67	33	108
6	35	50	53.4/73.7	53.7	23	0.5	72	19	101
7	25	50	51.9/72.5	54.8	20	0.3	74	35	102
8	35	60	61.3/79.4	62.4	20	0.1	50		131
9	35	73	74.5/87.7	70.8	19	0.3	54		155
10	15	73	76.3/89.1	73.8	18	0.3	54		160
11	60	73	75.4/88.2	72.0	19	0.1	39		151
12	35	80	81.9/91.7	82.5	18	0.1	46		179
13	35	90	92.2/96.6	91.6	20	0.1	47		231
14	35	100	100	100	21	0.4	69		334

[a] Concentration of monomers (w/v). [b] Related to total molar amount of monomers. [c] In weight percent based on PDD + TFE. [d] Determined during second heating: 25−400 °C; first heating: 25−300 °C; heating rate: 10 °C/min. [e] Copolymer insoluble in C_6F_6.

over dry ice. The concentration was determined by iodometry and was typically 11 wt %.

Copolymerization of Tetrafluoroethylene and PDD in CO_2. The experimental setup is shown in Figure 1. Polymerizations were conducted in a 25 mL high-pressure reaction view cell equipped with a stirring bar, thermocouple, rupture disk, and a sapphire window which permits visual observation of the reaction mixture with an endoscope. In a typical run (Table 1, no. 9) the high-pressure cell was purged with CO_2 to remove oxygen. Then the base of the cell was cooled to about 5 °C with an ice bath, and 4.08 g (16.7 mmol) of PDD was charged via a syringe while purging with argon. After sealing the cell the ice bath was removed, and 0.62 g (6.2 mmol) of TFE was introduced with a manual pump (HIP, model 62-6-10) under stirring. TFE was introduced as a mixture with CO_2 (50 wt %). To add a determined amount of TFE the pump was pressurized to 103 bar (1500 psig). The density of the TFE/CO_2 mixture at this pressure and a temperature of 25 °C is 0.91 g/mL. The necessary volume (1.36 mL) was introduced by repeated opening of the valve between the pump and the reaction view cell and repressurizing to 103 bar (1500 psig). During this procedure the temperature of the high-pressure view cell stayed below 10 °C. Then the reaction view cell was heated to 35 °C, and 0.27 mL of the initiator solution was transferred via syringe to a small tube connected to the CO_2 line. The reaction view cell was then pressurized to 138 bar (2000 psig) with additional CO_2 using an automatic syringe pump (ISCO, model 260 D) while simultaneously introducing the initiator. After 5 h, the CO_2 was slowly released and the residual copolymer in the high-pressure cell was extracted three times to 138 bar (2000 psig) with CO_2 to remove unreacted monomer and initiator residue.

Characterization. Glass transition temperatures were measured with a Seiko Instruments DSC 220 system under nitrogen. Heating rates for DSC measurements were 10 K/min. NMR spectra were measured of solutions in hexafluorobenzene (10 wt %) at room temperature. The ^{19}F NMR spectra were observed on a Bruker Avance 500 spectrometer operating at a frequency of 470.54 MHz with fluorotrichloromethane as internal standard. The resonance of hexafluorobenzene was presaturated. A 5 mm NMR tube with an insert filled with deuterated benzene was used as an internal lock. The parameters of the ^{19}F NMR nuclei were as follows: the 90° pulse was 8.40 μs, the sweep width was 50 000 Hz, the number of transients was 32, and the relaxation delay was 10 s. Viscosities were measured with an automated Ubbelohde viscometer (Schott) using Fluorinert FC-75 at 20 °C as the solvent. IR spectra were taken of polymer films on NaCl plates (Bruker IFS 66v/S). The films were cast from solutions in Fluorinert FC-75. For the subtraction spectra films were pressed at 200 °C.

Results and Discussion

Influence of Reaction Conditions on Polymer Properties. Copolymers of TFE and PDD were synthesized in CO_2 and characterized using NMR spectroscopy, FTIR spectroscopy, differential scanning calorimetry, and solution viscosity (Table 1). Compared to poly(tetrafluoroethylene), which is a highly crystalline polymer and insoluble in organic solvents below 300 °C, TFE/PDD copolymers of certain compositions are soluble in perfluorinated organic solvents like hexafluorobenzene, perfluorooctane, or Fluorinert FC-75 at room temperature which facilitates their characterization. ^{19}F NMR spectroscopy is a useful method to obtain quantitative information about the average composition and the microstructure of the synthesized copolymers. Spectra of solutions in hexafluorobenzene were measured whose resonance does not overlap with signals of the copolymer. As can be seen from Figure 2, there are at least two signals for the CF_3 groups of the PDD monomer unit. The relative intensities of the resonances depend on the copolymer composition. These signals could be due to different comonomer sequence distribu-

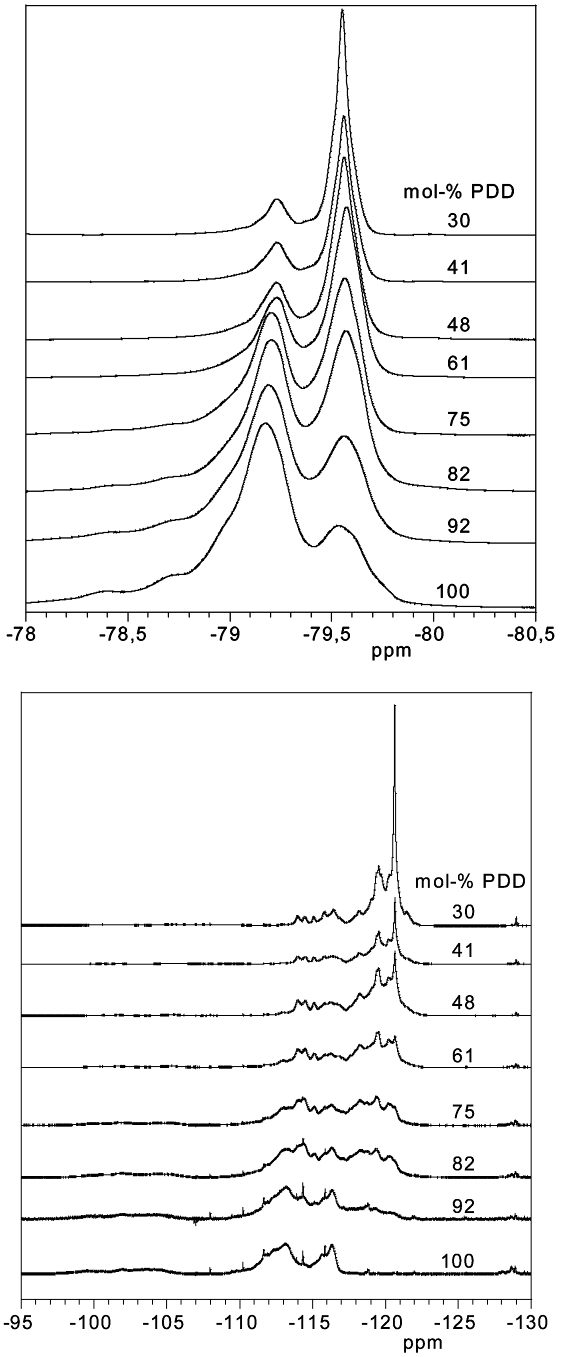


Figure 2. Comparison of the CF_3 and CF, CF_2 resonances in the ^{19}F NMR spectra of TFE/PDD copolymers with different compositions.

tions but also configurational isomerism of the cyclic ring structure of the PDD monomer unit. Cylic olefins like PDD can be treated as 1,2-disubstituted ethylenes. The polymerization results in a polymer structure with two different stereocenters in the repeating unit. For the PDD homopolymer four different stereoregular structures are possible, which are shown in Scheme 2. In contrast to 1,2-disubstituted ethylenes, cyclic structures in addition show cis–trans isomerism for the chain bonds entering and leaving the ring. The erythro polymers show a cis configuration of the polymer chain and are chiral whereas the threo polymers have a trans configuration and are achiral. If the two signals of the CF_3 groups were due to different comonomer sequences, they should be at least sensitive to the triad level and three signals for the CF_3 groups would be expected. This possibility can further be excluded because in the spectrum of the PDD homopolymer at least two signals are present. The CF_3 groups are therefore probably sensitive to a cis or trans configuration of the PDD monomer unit in the polymer chain. The resonances of the CF and CF_2 groups are very broad and not resolved. The broadness is determined by the transverse relaxation time T_2, which is related to the tumbling rate of molecules and the segmental mobility of the polymers. Since PDD/TFE copolymers are very stiff due to the decreased rotational flexibility of the in-chain ring structure, the segmental mobility is low, resulting in short relaxation times T_2 which broaden signals. The average copolymer composition was calculated from the area of the CF_3 (A_1) and the CF and CF_2 resonances (A_2) according to eq 1,

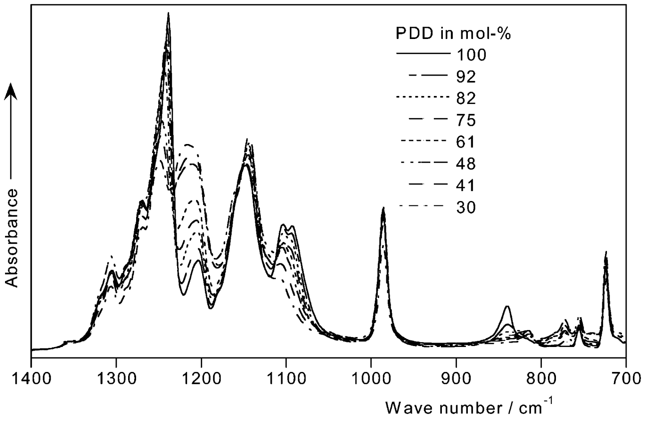
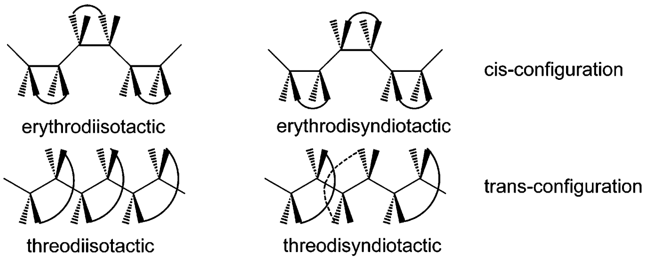


Figure 3. IR spectra of copolymers with various compositions.

Scheme 2. Stereoregular Configurations for PDD Homopolymer



$$x_{\mathrm{PDD}} = \frac{2A_1}{3A_2 + A_1} \qquad (1)$$

where x_{PDD} is the mole ratio of PDD monomer units in the polymer. A comparison of the IR spectra of copolymers with varying PDD content (Figure 3) shows significant changes. The intensity of the absorbance at ~1247 cm^{-1} for example increases with increasing PDD content whereas the band at ~1212 cm^{-1} decreases. Attempts to relate these changes to copolymer composition were successful with a method shown in Figure 4. The height of the absorbances from a baseline through the points at 1400 and 925 cm^{-1} and the maximum of the aborbance at ~1212 and ~988 cm^{-1} were determined, and the ratio was plotted against the PDD content obtained from the ^{19}F NMR spectra. Figure 5 shows the calibration curve which allows the determination of the copolymer composition using IR spectroscopy. For the ratio L_2/L_1, a linear relation between this ratio and the copolymer composition could be obtained.

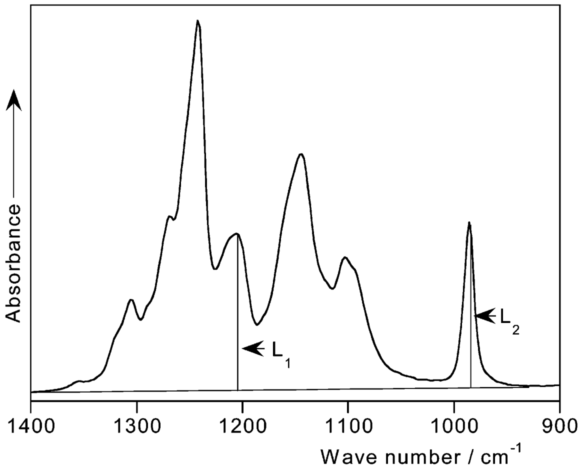


Figure 4. IR method for determination of PDD content.

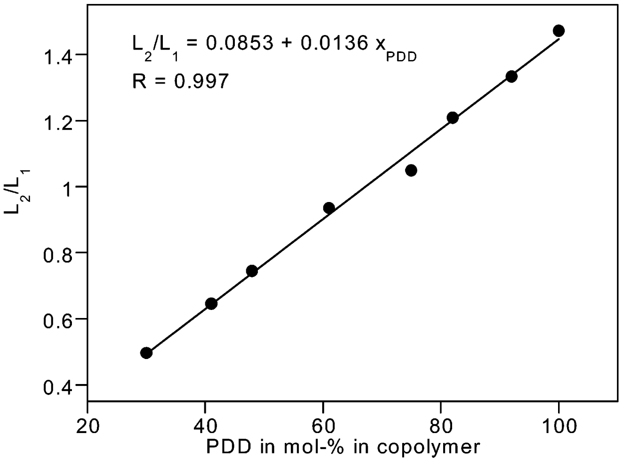


Figure 5. Calibration curve for the calculation of the PDD content obtained form ^{19}F NMR spectroscopy.

The reaction conditions were systematically varied to investigate the influence of initiator concentration, temperature, and feed composition on the copolymer properties. In a series of experiments (Table 1, no. 4−6) the initiator concentration was varied while keeping the other conditions constant. The reactions were carried out at an initial pressure of 138 bar (2000 psig) at 35 °C with a feed ratio of 50 mol % PDD and a monomer concentration ranging from 21 to 24% (w/v). As expected, the molecular weight of the polymers was found to decrease with increasing initiator concentration. The intrinsic viscosities ranged from 19 to 80 mL/g for an initiator concentration of 0.5 and 0.1 mol %, respectively. The yield showed an opposite trend, increasing with increasing initiator concentration from 34% at an initiator concentration of 0.1 mol % to 72% at a concentration of 0.5 mol %. Reducing the reaction temperature to 25 °C resulted in a slightly higher yield and molecular weight (Table 1, no. 7) compared to the reaction run at 35 °C (Table 1, no. 5). The glass transition temperatures for the copolymers synthesized with a feed composition of 50 mol % PDD varied between 101 and 109 °C.

A series of experiments were carried out at different feed compositions to investigate the influence of the copolymer composition on the glass transition temperature (Table 1, no. 1−4, 8−9, 12−14) while keeping the other conditions constant. No melting peaks were observed in the DSC traces for any of the copolymers. The lowest T_g of 67 °C was obtained at a feed composition of 20 mol % PDD. Since the copolymer was insoluble in hexafluorobenzene, the copolymer composition could not be obtained. The insolubility is probably due to TFE runs of sufficient length, which results in a small amount of crystallization, although no melting transition was easily discernible by DSC. With increasing PDD content the copolymers become amorphous and are soluble in perfluorinated organic solvents. The glass transition temperature increases strongly because there is less conformational flexibility due to the fixed and bulky ring structure of the dioxole monomer unit. The T_g reaches the highest value for the PDD homopolymer with a T_g of 334 °C. As can be seen from Figure 6, the slope of the curve increases strongly at higher PDD contents. Intermolecular polar interactions between the CF_3 groups of the PDD monomer units probably also contribute to an increase of the glass transition temperature at high PDD contents.

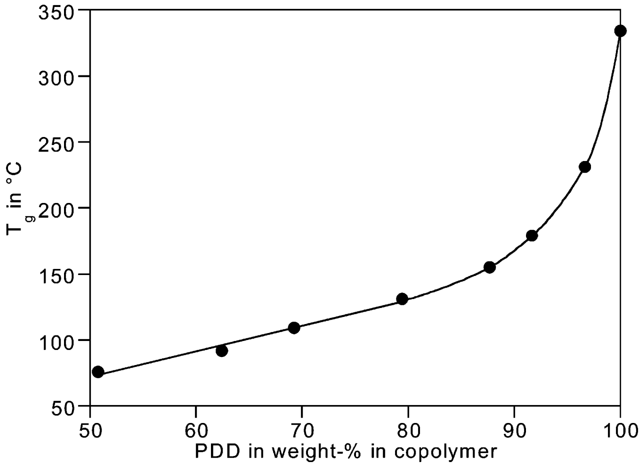
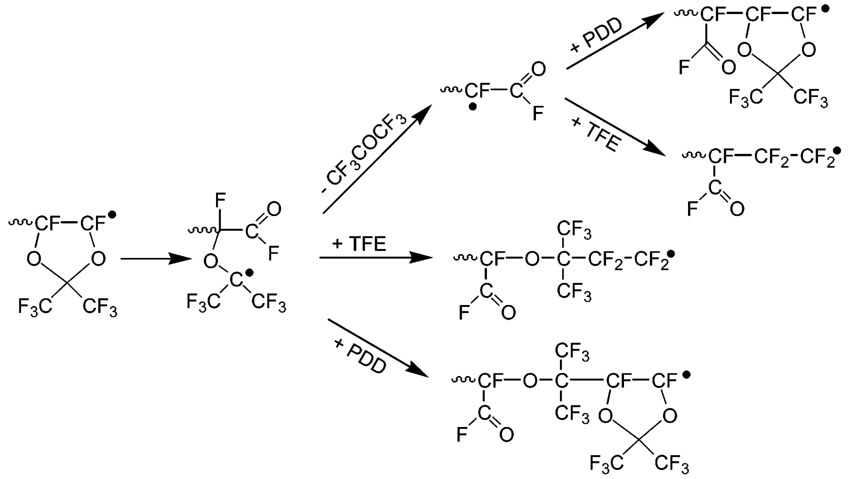


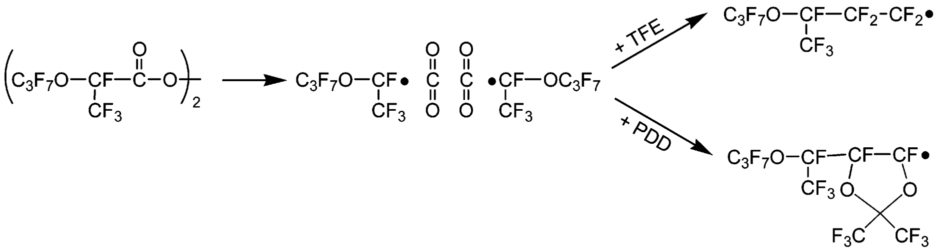
Figure 6. Dependence of the glass transition temperature on the copolymer composition.

Phase Behavior. The phase behavior during polymerization was studied by visual observation with an endoscope. A homogeneous one-phase system was observed initially for all of the reactions reported. However, during the polymerization a change in the phase equilibrium was observed in some cases as a function of the feed composition and the temperature. At very high and very low PDD contents in the feed (20, 90, and 100 mol %; Table 1, no. 1, 13, and 14) and at a reaction temperature of 35 °C, the copolymer precipitated during the course of the polymerization. At feed compositions between 40 and 73 mol % PDD (Table 1, no. 3, 4, 8, and 9), phase separation was also observed forming two clear phases. The lower phase was the polymer-rich phase. The upper phase was the CO_2-rich phase, but upon venting it was apparent that some polymer was indeed soluble in this upper phase as precipitates were seen. The final product looked as if it was heated above T_g and formed a foam upon venting which shows that CO_2 acts as a plasticizer. The same behavior was found at a higher reaction temperature of 60 °C (Table 1, no. 11) and a feed composition of 73 mol % PDD. The phase behavior was different at a lower reaction temperature of 15 °C (Table 1, no. 10). No phase separation was observed. This was also the case at intermediate feed compositions of 30 and 80 mol % PDD (Table 1, no. 2 and 12). The reaction appeared to occur as a clean, homogeneous solution polymerization in CO_2. An interesting behavior was found during the synthesis of the PDD homopolymer. The polymer did not precipitate but

Scheme 3. Side Reaction That Can Occur during the Copolymerization Which Would Lead to Deleterious Unstable End Groups



Scheme 4. Thermal Decomposition of Bis(perfluoro-2-*N*-propoxypropionyl) Peroxide



formed a gel which filled the whole reactor volume. After release of CO_2 a fine white powder remained.

The solubility of a polymer in a solvent depends on the energy and entropy of mixing and for CO_2 also on the CO_2 density. CO_2 has shown to plasticize many polymers and even dissolve amorphous fluoropolymers due to favorable interactions between the C−F bonds in the polymer and CO_2. The entropy of mixing is associated with the difference in free volume between polymer and solvent[16] and the stiffness of the polymer chain. The entropy of mixing becomes more negative with decreasing rotational flexibility of the copolymer. At low PDD contents there are TFE runs of sufficient length in the copolymer to result in crystallization. This explains the insolubility of TFE/PDD copoylmers with high amounts of TFE. With increasing PDD content the copolymer becomes amorphous. At the same time the rotational flexibility of the copolymer is decreased, and the entropy of mixing becomes more negative. On the other hand, the free volume of the copolymer increases, which promotes solubility. These two competing effects could give an explanation for the complex phase behavior between 30 and 80 mol % PDD. It also must be taken into account that unreacted monomer influences solubilities. At very high PDD contents the copolymer becomes again insoluble. The reason for this is probably not only a greater stiffness of the chain but also strong polar intermolecular interactions between the CF_3 groups in the 2-position of the dioxole monomer unit. These interactions favor polymer segment−polymer segment over polymer segment−CO_2 interactions. Another explanation for the decreased solubility could be the formation of microcrystalline regions. Although no melting peaks were observed by DSC, perhaps a more sensitive technique such as wide-angle X-ray scattering could be used to confirm the existence or absence of crystallization.

Comparison of Teflon AF 1601 with Copolymer Synthesized in CO_2. For the investigation, two commercial samples of Teflon AF 1601, a fluorinated and unfluorinated one, were compared with a TFE/PDD copolymer synhesized in carbon dioxide having a similar molecular weight and glass transition temperature. Commercially available Teflon AF is typically fluorinated to remove thermally unstable end groups. The intrinsic viscosities were 35 and 40 mL/g and the glass transition temperatures 155 and 157 °C for the copolymer synthesized in CO_2 and Teflon AF 1601, respectively. Special attention was focused on the formation of thermally unstable groups. Such groups can produce bubbles or voids upon melt fabrication. Acid fluoride groups, which can hydrolyze, can form because of the competing side reactions shown in Scheme 3. Moreover, initiator fragments incorporated as end groups in the polymer chain can influence the thermal stability of fluoropolymers.[17]

The copolymerization in carbon dioxide was carried out at a low reaction temperature of 35 °C to suppress the above-described side reaction. Bis(perfluoro-2-*N*-propoxypropionyl) peroxide was used as the initiator. The decomposition of this initiator proceeds via a single-bond homolysis mechanism,[13] resulting in the formation of perfluorinated end groups which are known to be thermally stable (Scheme 4). The initiator has a half-life time of 40 min at 35 °C.[13]

IR spectroscopy is a very sensitive method for the determination of −COF or −COOH groups in fluorinated polymers. To look for differences the compared spectra were subtracted. The subtraction technique is illustrated in Figure 8. As reference a fluorinated commercial product (Teflon AF 1601) was used. As can be seen from the subtracted spectrum in Figure 8, the unfluorinated commercial sample shows significant differences compared to the fluorinated one. Additional

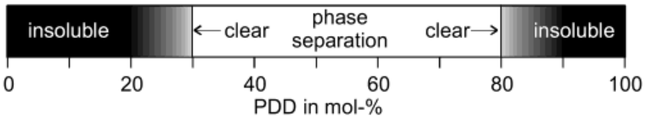


Figure 7. Phase behavior during copolymerization of PDD and TFE ($T = 35$ °C).

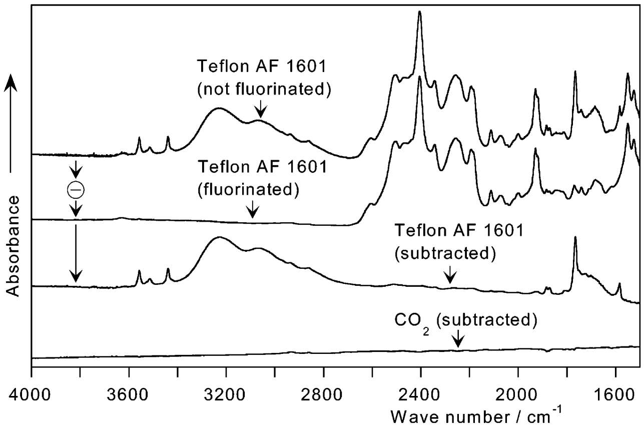


Figure 8. Comparison of the FTIR spectra of a PDD/TFE copolymer synthesized in CO_2 (75 mol % PDD) and fluorinated and not fluorinated Teflon AF 1601 (74 mol % PDD).

Table 2. Assignments of IR Absorptions

wavenumber (cm^{-1})	group	assignment[a]
3557	COOH	ν(OH), free
3514	*b*	
3439	$CONH_2$	$\nu(NH_2)$ symm
3400−2700	COOH	ν(O−H) stretching, bonded
1884	COF	ν(C=O)
1872	*b*	
1811	COOH	C=O stretching, free
1765	COOH	C=O stretching, bonded
1583	$CONH_2$	δ(N−H)

[a] Assignments according to Pianca et al.[17] [b] Unknown.

absorptions for hydrogen-bonded and free COOH-groups in the region of the C=O and O−H stretching frequencies are present in the spectrum of the unfluorinated product. The assignments were made according to the literature[17] and are given in Table 2. Besides COOH groups there are also signals due to $CONH_2$ groups. These groups can form if ammonium salts are present in the reaction mixture. The spectra of the fluorinated commercial sample and the sample synthesized in CO_2 are very similar. The subtraction results in an almost straight line. The similarity of both copolymers was confirmed with ^{19}F NMR spectroscopy (Figure 9). The spectra are almost identical, indicating a similar microstructure. An additional resonance can be seen in the spectrum of the CO_2 sample at −81.3 ppm, which is not present in the commercial product. This signal could be due CF_3 groups formed because of a side reaction or CF_3 groups of initiator fragments incorporated as end groups in the copolymer. Since no evidence for a side reaction could be found, the latter possibility is probably right. The results show that copolymers with properties comparable to those of the fluorinated commercial product could be synthesized directly in carbon dioxide without the need for an expensive fluorination step. No significant difference could be found using IR spectroscopy, NMR spectroscopy, and differential scanning calorimetry.

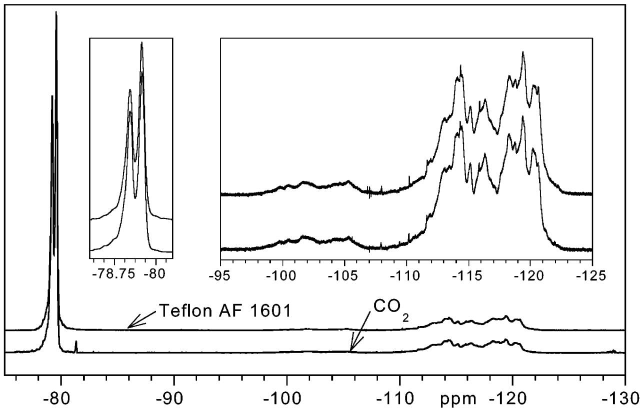


Figure 9. Comparison of the ^{19}F NMR spectra of a PDD/TFE copolymer synthesized in CO_2 (75 mol % PDD) and fluorinated and not fluorinated Teflon AF 1601 (74 mol % PDD).

Conclusion

TFE/PDD copolymers were synthesized in CO_2 at low temperatures, and the phase behavior was investigated for the first time. The molecular weight was adjustable by changing the initiator concentration. Copolymers with different compositions were prepared having a broad range of glass transition temperatures from 67 to 334 °C. The phase behavior was influenced by the feed composition. At very high and very low PDD contents in the feed, the polymer precipitated at an initial pressure of 2000 psig (138 bar). Between 40 and 73 mol % PDD the reaction mixture phase separated during the reaction whereas at 30 and 80 mol % PDD no phase separation was observed. No difference could be found between a fluorinated commercial sample (Teflon AF 1601) and a copolymer synthesized in CO_2 having a similar composition using ^{19}F NMR spectroscopy, IR spectroscopy, and differential scanning calorimetry. A simple method to determine the copolymer composition based on infrared spectroscopy has been developed. The synthesis of the copolymers in CO_2 has several advantages compared to conventional polymerization techniques: The low reaction temperature and the use of a perfluorinated initiator potentially results in a copolymer whose properties are comparable to those of the fluorinated commercial product. An additional fluorination step is therefore unnecessary. The product is obtained in dry and pure form without contaminant from solvent or surfactants. Moreover, the use of TFE/CO_2 mixtures instead of pure TFE improves the safety of the polymerization process.

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