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Synthesis and Property of Well-Defined Copolymer of Chlorotrifluoroethylene and *N*-Vinylpyrrolidone by Xanthate-Mediated Radical Copolymerization under ^{60}Co γ-ray Irradiation

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Living/controlled radical copolymerization of chlorotrifluoroethylene and *N*-vinylpyrrolidone has been successfully achieved at room temperature under ^{60}Co γ-ray irradiation in the presence of ethyl 2-(ethoxycarbonothioylthio) acetate. The living/controlled character of the polymerization was confirmed by GPC and NMR analyses, as well as the chain extension polymerization. The physical property of the obtained polymers was investigated and the experimental results indicate that the fluorinated copolymer showed excellent film-forming characteristic and high mechanical property. Moreover, the fluorinated amphiphilic block copolymers prepared by chain extension polymerization show good biocompatibility.

Introduction

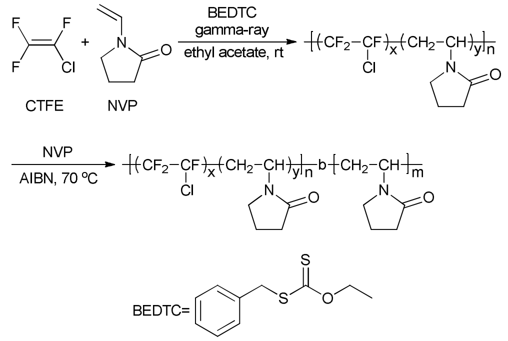
Since the first perfluoropolymer, polytetrafluoroethylene (PTFE) was invented by DuPont Company, fluorinated polymers have attracted more and more attention in the polymer science field. The fluorinated polymers exhibit many unique high-performance features, such as low surface energy, low dielectric constants, low refractive index, long durability, high-thermal stability, and chemical inertness (to acids, bases, solvents, and petroleum), owing to high electronegativity of fluorine atom and the strong dissociation energy of C-F bond. Therefore, the fluorinated polymers have been widely explored and applied in many areas, including protective coatings, fuel cell membranes, novel elastomers, and microelectronics.[1]

Due to the poor solubility in common organic solvents and difficult crosslinking of perfluoropolymers, more and more research works focus on the copolymerization of fluoroolefins and non-fluoromonomer to make semi-fluorinated polymers in recent years.[2-19] Chlorotrifluoroethylene (CTFE) is one of the most commonly used fluoroolefins and the copolymerization of CTFE with other vinyl monomers has been extensively investigated. Since CTFE is an electron-deficient monomer (e=1.56)[6], alternating copolymers are generally obtained when it is copolymerized with electron-rich vinyl monomers, such as ethylene[12-14] and vinyl ethers.[6,9,15-18]

Since 1990s, methods of living/controlled radical polymerization, including nitroxide-mediated polymerization (NMP),[21] atom transfer radical polymerization (ATRP),[22] and reversible addition-fragmentation chain transfer (RAFT) polymerization,[23] have been extensively studied and developed as a powerful tool for the synthesis of well-defined polymers with predetermined molecular weight, narrow molecular weight distribution, and various architectures. However, there are few papers reported on the living/controlled radical polymerization of CTFE with other monomers until now, which may be attributed to the gaseous state and the unique chemical properties of CTFE. In 2003, Wang and his coworkers[3] reported the synthesis of a hyperbranched fluoropolymer based on CTFE and p-chloromethyl styrene via self-condensing vinyl polymerization (SCVP) termed by Frechet et al[24]. The results showed that the molecular weights of the polymers increased with monomer conversions and the polymer was soluble in common organic solvents, but no more information about the features of living/controlled radical polymerization was given. In 2011, our group successfully achieved the living/controlled free radical copolymerization of CTFE and butyl vinyl ether (BVE) at room temperature under ^{60}Co γ-ray irradiation with an *O*-ethyl xanthate.[9] However, the obtained alternating copolymer exhibits very low glass transition temperature (T_g, -8 °C),[6] which severely limit its applications due to the viscous state at room temperature.

Poly(*N*-vinylpyrrolidone) (PVP) has attracted the constant attention of researchers from both academic and industrial worlds since its invention was declared in 1941.[25] Its unique features, such as exceptional film-forming and adhesive characteristics, pH-stability, nontoxicity and biocompatibility undoubtedly position PVP as one of the most interesting polymers. Since *N*-vinylpyrrolidone (NVP) is an electron donating monomer (e=-1.62),[26] it tends to form alternating copolymer with electron withdrawing monomer CTFE. Moreover, reversible addition–fragmentation/macromolecular design by interchange of xanthates (RAFT/MADIX) polymerization was found to be a suitable approach to deactivate PVP chain growth in a reversible manner, thereby giving access to PVP-based controlled architectures.[27–36] *O*-ethyl xanthates are generally used as the RAFT/MADIX agents, due to their high efficiency both in controlling molecular weights and yielding narrowly dispersed PVP up to high conversion. However, so far as we know, there is no paper published on living/controlled radical copolymerization of NVP and CTFE.

In this article, we report the living/controlled radical polymerization of CTFE and NVP under ^{60}Co γ-ray irradiation with *S*-benzyl *O*-ethyl dithiocarbonate (BEDTC) as the RAFT/MADIX agent at room temperature (Scheme 1). Polymerization results reveal that molecular weights of the copolymers are controlled and the molecular weight distributions are narrow. Molar fractions of CTFE unit in the copolymer increase with the initial molar ratios of CTFE to NVP and the conversions. Moreover, the obtained fluorinated copolymer showed excellent film-forming characteristic and high mechanical properties. Furthermore, a fluorinated amphiphilic block copolymer with no cytotoxicity was prepared by chain extension polymerization with NVP.



Scheme 1 Schematic representation of RAFT/MADIX copolymerization of CTFE and NVP under ^{60}Co γ-ray irradiation at room temperature and the chain extension polymerization of the copolymer.

Experimental

Materials

Chlorotrifluoroethylene (CTFE) was purchased from Zhejiang Juhua Co., Ltd, China. *N*-vinylpyrrolidone (NVP) was obtained from Aladdin Industrial Corporation (Shanghai, China), which was dried with CaH_2, and distilled under reduced pressure before use. Ethyl acetate, diethyl ether and isopropanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethyl acetate was refluxed and distilled over CaH_2. Bull serum albumin (BSA), Dulbecco's modified Eagle's medium (DMEM, Hyclone), fetal bovine serum (FBS, Hyclone) were used as obtained. BEDTC was synthesized according to a previous literature.[29] All other chemicals were used as received unless otherwise noted.

Characterization

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer, using $CDCl_3$ as a solvent. The values of the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by means of a Waters 150C gel permeation equipped with 10^3, 10^4, and 10^5 Å Waters Ultrastyragel columns and light scattering detector, using THF (1.0mL/min) as the eluent, and the calibration was carried out with polystyrene standards. Weight percentages of carbon, hydrogen and nitrogen atoms were assessed by elemental analysis on a Vario EL cube (Elementar, Germany) instrument. Thermogravimetric analyse (TGA) was performed with a DTG-60H apparatus from Shimadzu, under air, at the heating rate of 10 ^{o}C min^{-1} from room temperature up to a maximum of 500 ^{o}C. Stress-strain curves were recorded on a DMTAQ800 (TA, America) instrument at 25 ^{o}C, and each sample was characterized for three times, and the results were averaged..

Exemplary procedure for RAFT/MADIX copolymerization of CTFE and NVP

The reaction was performed in a stainless steel autoclave equipped with a manometer, a safety inlet valve, and a magnetic stirrer. First, a mixture of 7.9 mg BEDTC (0.037 mmol), 0.40 ml NVP (3.7 mmol) and 5.0 mL ethyl acetate was introduced into the autoclave. Then the vessel was closed and immersed in the liquid nitrogen for 15 min. After several nitrogen-vacuum cycles to remove any traces of oxygen, required quality of CTFE was condensed into the autoclave via a mass flow meter and the exact value was assessed by double weighing (the difference of weight before and after filling the autoclave with CTFE). The polymerization was carried out at room temperature under ^{60}Co γ-ray irradiation (2 Gy/min) for a predetermined time, and then quenched by cooling with ice water. The unreacted CTFE was slowly vented. The solution was concentrated and precipitated in diethyl ether. The polymer was finally dried under vacuum at 40 ^{o}C until a constant weight was attained and the conversion of the monomer was determined by elemental analysis and gravimetry.

Procedure for chain extension polymerization with NVP

Poly(CTFE-co-NVP) (0.102 g, 0.011 mmol) bearing a xanthate end-group as a macro chain transfer agent (macro-CTA) was solved in 5 mL ethyl acetate and charged in a 10 mL glass tube with 1.3 mg AIBN (0.008 mmol), as well as 1.00 mL NVP (9.31 mmol). Three cycles of freeze-vacuum-thaw were conducted to remove any traces of oxygen. After sealed under vacuum, the tube was immersed in thermostatic oil bath at 70 ^{o}C for 6 h. Then the tube was cooled down by ice water to stop the polymerization and the solution was precipitated into diethyl ether. Purification was carried out by repeating dissolution in ethyl acetate and precipitation from diethyl ether. The resultant polymer was collected and dried under vacuum at 40 ^{o}C until a constant weight.

Exemplary procedure for film preparation

Poly(CTFE-co-NVP) films were prepared by casting from 10 wt% ethyl acetate solutions onto glass plates, drying at 30 ^{o}C for 12 h, followed by further drying at 40 ^{o}C for 24 h in a vaccum oven to remove any residual solvent.

In vitro cytotoxicity

Cell viability was examined by the MTT assay. L929 cells were seeded in a 96-well plate at a density of 1×10^4 cells per well and incubated in DMEM supplemented with 10% FBS overnight. After the media was refreshed, the cells were treated with the fluorinated amphiphilic block copolymer solution at a given concentration. The treated cells were incubated in a humidified environment with 5% CO_2 at 37 ^{o}C for 24 h, then MTT reagent (in 20 μL PBS buffer, 5 mg/mL) was added to each well, and the cells were further incubated for 4 h at 37 ^{o}C.

The culture medium in each well was removed and replaced by 100 μL isopropanol. The plate was gently agitated for 15 min, and the absorbance values were recorded at a wavelength of 570 nm upon using a Thermo Multiskan flash. The cell viability is calculated as $A_{570,\text{treated}}/A_{570,\text{control}}\times 100\%$, where $A_{570,\text{treated}}$ and $A_{570,\text{control}}$ are the absorbance values with or without the addition of polymer, respectively. Each experiment was done in quadruplicate. The data are expressed as average ± standard deviations (±SD).

Results and discussion

RAFT/MADIX copolymerization of CTFE and NVP

The results of RAFT/MADIX copolymerization of CTFE and NVP under ^{60}Co γ-ray irradiation (2 Gy/min) with BEDTC as the chain transfer agent at room temperature are shown in Table 1. Equations (1) and (2) are used to determine the molar fractions of NVP and CTFE in the copolymer (NVP% and CTFE%, respectively):

$$\mathbf{N\%} = \frac{\mathbf{NVP\%\times M_{N}}}{\mathbf{NVP\%\times M_{NVP}+CTFE\%\times M_{CTFE}}} \tag{1}$$

$$\text{CTFE\%=1-NVP\%} \tag{2}$$

where N% is the weight percent of N in the copolymer accessed by elemental analysis. M_{CTFE} and M_{NVP} stand for the molecular weight of CTFE and NVP, respectively. M_N is the atomic weight of nitrogen.

The theoretical molecular weights ($M_{n,th}$) of poly(CTFE-co-NVP) are calculated according to equation (3):

$$M_{n,th}=100\times\text{Conv.}\times[M_{NVP}+(\text{CTFE\%/NVP\%})\times M_{CTFE}]+M_{BEDTC} \tag{3}$$

where 100 is the initial molar ratio of NVP to BEDTC. Conv. is the conversion of NVP. M_{CTFE}, M_{NVP}, and M_{BEDTC} stand for the molecular weight of CTFE, NVP and BEDTC, respectively.

Table 2~~1~~ Results of the RAFT/MADIX copolymerization of CTFE and NVP under ^{60}Co γ-ray irradiation (2 Gy/min).

Sample	Time/min	$[CTFE]_0/[NVP]_0$ [b]	Elemental analysis (wt %)			Copolymer composition (mol %)		Conv.[a]	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n [c]
			C	H	N	CTFE	NVP				
P1	120	1	44.5	4.92	6.71	45.6	54.4	0.425	9,100	ND[d]	ND
P2	120	2	43.4	4.71	6.45	47.6	52.4	0.421	9,300	ND	ND
P3	120	3	43.2	4.62	6.37	48.3	51.7	0.416	9,400	ND	ND
P4	120	4	43.1	5.14	6.34	48.5	51.5	0.409	9,200	15,800	1.45
P5	30	4	44.3	4.93	6.62	46.3	53.7	0.130	3,000	9,700	1.43
P6	60	4	44.0	4.80	6.57	46.7	53.3	0.247	5,500	11,900	1.45
P7	180	4	42.6	4.70	6.20	49.6	50.4	0.525	12,100	18,500	1.41
P8	240	4	42.6	4.62	6.19	49.7	50.3	0.562	12,900	19,600	1.44

[a] Conversion of NVP determined by gravimetry and elemental analysis. [b] Initial molar ratio of CTFE to NVP. [c] Molecular weight distribution determined by GPC. [d] Not determined.

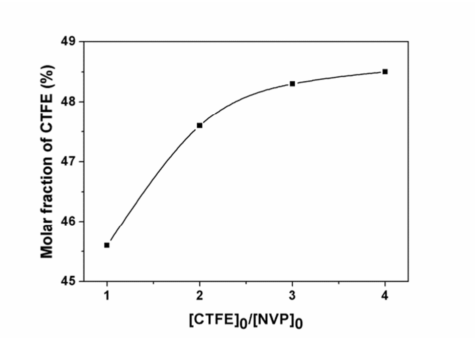
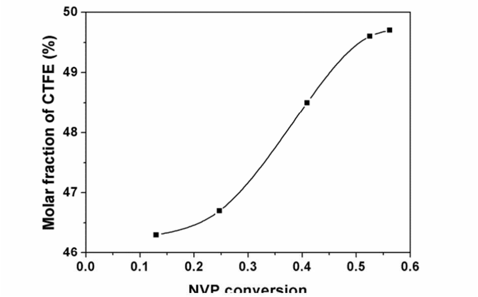


Fig. 1 Molar content of CTFE in the copolymer as a function of initial molar ratio of CTFE to NVP (P1, P2, P3 and P4).

It can be seen that in Table 1, the composition of the obtained polymer is very close to that of the alternating copolymer, which is related to the ratio of the two monomers in the feed. As shown in Fig.1, molar fractions of CTFE in the resulted copolymers increase with the initial molar ratio of CTFE to NVP (P1, P2, P3 and P4,) in a certain polymerization time under the same reaction condition. However, this trend level off when $[CTFE]_0/[NVP]_0$ reaches up to 3.



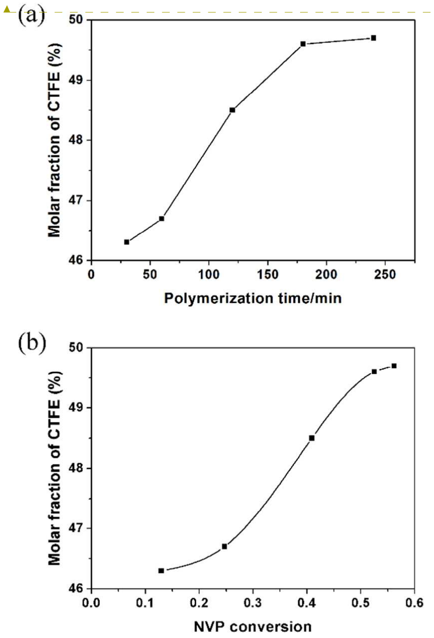


Fig. 2 Molar content of CTFE in the copolymer as a function of (a) polymerization time and (b) NVP conversion (P4, P5, P6, P7 and P8).

On the other hand, when the initial molar ratio of CTFE to NVP is fixed, molar fractions of CTFE in the resulted copolymers increase with polymerization time and the monomer conversions (P4, P5, P6, P7 and P8, shown in Fig. 2), due to the increasing of real-time molar ratio of CTFE to NVP in the polymerization process.

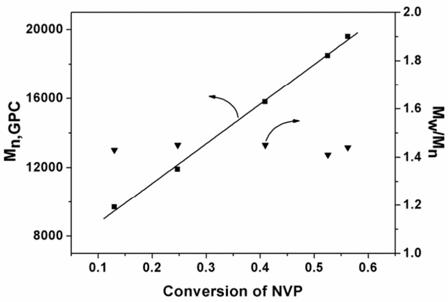


Fig. 3 Molecular weight and molecular weight distribution as a function of NVP conversion for the copolymerization of CTFE and NVP.

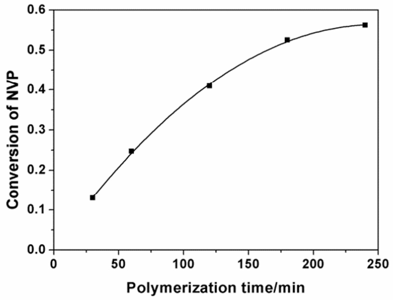


Fig. 4 NVP conversion as a function of polymerization time for the copolymerization of CTFE and NVP.

It can be observed that the molecular weights of poly(CTFE-co-NVP) increase linearly with the monomer conversions and the molecular weight distributions (M_w/M_n) keep narrow up to high conversions (Fig. 3). However, the molecular weights determined by GPC ($M_{n,GPC}$) are higher than the theoretical values (a directly comparison is shown in Fig. S3 in ESI), this is probably due to using the polystyrenes as the standards in the calibration. Fig. 4 shows the relationship between NVP conversion and polymerization time, which is consistent with the living/controlled radical polymerization.

The structure of the copolymer was characterized by ^1H and ^{19}F NMR spectroscopy, and sample P4 was chosen as a representative. As mentioned above, copolymerization of CTFE and BVE forms quasi-alternating copolymers under the reaction condition in this work. For sample P4, the molar ratio of CTFE to NVP in the copolymer is 48.5/51.5, which is very close to the perfect alternating structure. Fig. 5a shows the ^1H NMR spectrum of poly(CTFE-co-NVP).The resonances centered at 5.66 and 5.40 ppm can be attributed to the proton of methine in the structure of –CTFE–CH_2–C**H**R–CTFE– , R is the pendent group of NVP and the split arises from the attached chiral carbon. The broad peaks located at 2.83 ppm (partially overlapped with the neighbouring peaks) are ascribed to the methylene of the NVP units in the polymer backbone. And the resonances at 3.45, 2.34, and 2.04 ppm belong to the pendent group of NVP unit. In addition, the peaks appeared at 7.35 ppm

Formatted: Font: Times New Roman, 9 pt belong to the phenyl end group from BEDTC, indicating chain transfer reaction occurred via RAFT process. Signals of the end groups (ethoxyl groups) are overlapped with those of the NVP units. ^{19}F NMR spectrum (Fig. 5b) shows a series of multiplets centered at -105.8, -115.3, -120.9, and -125.8 ppm, which can be designated to the groups of **CF_2** and **CFCl** in the chain backbone. Furthermore, the absence of peak at -100 ppm in ^{19}F NMR spectrum bears witness that there is no CTFE-CTFE diads in the polymer chains.[38]

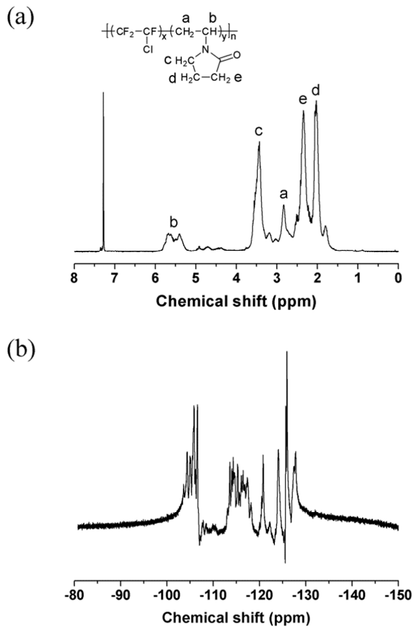


Fig. 5 (a) ^{1}H and (b) ^{19}F NMR spectra of poly(CTFE-co-NVP) (P4) recorded in $CDCl_3$ at room tempreture.

Chain extension polymerization with VAc

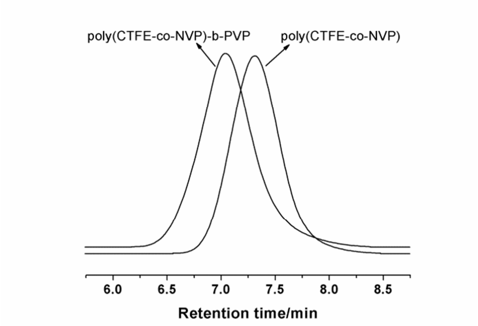


Fig. 6 GPC traces of poly(CTFE-co-NVP) (P4, $M_{n,GPC}$=15800, M_w/M_n=1.45) and poly(CTFE-co-NVP)-b-PVP ($M_{n,GPC}$=27600, M_w/M_n=1.49).

Chain extension polymerization was conducted with poly(CTFE-co-NVP) (P4 inTable 1) as a macro-CTA and NVP as the monomer. Fig. 6 shows the GPC traces of the block copolymer (poly(CTFE-co-NVP)-b-PVP) and the macro-CTA, respectively. A symmetrical and monomodal curve for the block copolymer shifts toward higher molecular weight compared with the curve of the macro-CTA in the GPC traces and this result indicates that the chain extension polymerization has been successfully achieved. Moreover, the molecule weight distribution is still narrow (M_w/M_n=1.49). These data provide additional evidence for the living/controlled polymerization.

Preparation and properties of poly(CTFE-co-NVP) films

The colorless and transparent films of poly(CTFE-co-NVP) were prepared by solution casting and the stress-strain property of the films was characterized on a dynamic mechanical thermal analyzer. Fig. 7 shows that the tensile strength of the film increases with the molecular weight of the copolymer. Note that the tensile stress of the film (sample P8) with a molecular weight of 12900 was measured to be 49.02 MPa, which is ~~higer~~ higher than that of PTFE (about 25-30 MPa). Moreover, the stress of the film is related to its ~~stain~~ strain as shown in Fig. 8.

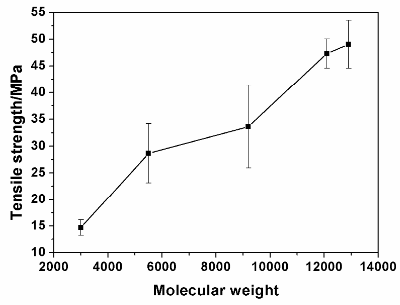


Fig. 7 Tensile strength as a function of $M_{n,th}$ of the copolymer (P4, P5, P6, P7 and P8).

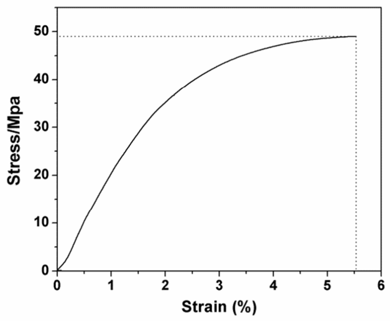


Fig. 8 Stress-strain curve of the film cast from P8 copolymer.

Thermal stability of the block copolymer was examined by thermogravimetric analysis (TGA) under air condition. Fig. 9 shows the thermogram of the copolymer P8. There were two steps in the TGA curve of the fluorinated copolymer through analysis. A small weight loss (about 15%) appears at above 150 °C, and another severe degradation starts from about 300 °C. which demonstrates that the block copolymer has good thermal stability.

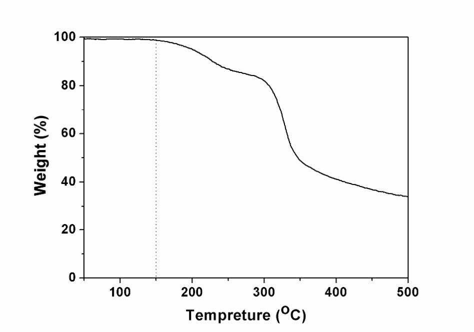
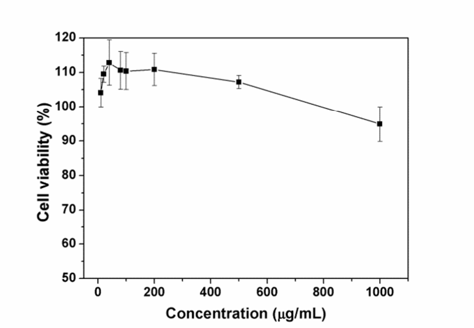


Fig. 9 TGA thermogram (under air, at 10 °C·min^{-1}) of sample P8.

In vitro cytotoxicity of the fluorinated amphiphilic block copolymer



~~**Fig. 10** Cytotoxicity of the fluorinated amphiphilic block copolymer in L929 cells.~~

Biocompatibility of the fluorinated amphiphilic block copolymer was preliminarily investigated. ~~It can be seen from Fig. 10 that the fluorinated amphiphilic block copolymer (poly(CTFE-co-NVP)-b-PVP) is biocompatible.~~ It shows almost no cytotoxicity up to a high polymer concentration of 1000 μg/mL (Fig. S4 in ESI). This means that the fluorinated copolymer could be used as a potential biomaterial for many biomedical applications.

Conclusions

Living/controlled radical copolymerization of CTFE and NVP has been successfully achieved under ^{60}Co γ-ray irradiation with *S*-benzyl *O*-ethyl dithiocarbonate (BEDTC) as the chain transfer agent at room temperature. Molar fractions of CTFE unit in the copolymer increase with the initial molar ratios of CTFE to NVP and the polymerization conversions. The obtained fluorinated copolymers showed excellent film-forming characteristic, and the formed films have really high strength and thermal stability, which makes them potential material for many applications, such as protective coating, membrane material, and even artificial blood vessel. Furthermore, a fluorinated amphiphilic block copolymer was prepared by chain extension polymerization of NVP and the experimental result of Cell viability in vitro demonstrated that the polymer has no significant cytotoxicity. Therefore, the amphiphilic block copolymer is expected to be a new potential polymer material for biomedical applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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