# Reversible Addition-Fragmentation Chain Transfer Graft Polymerization of Acrylonitrile onto PE/PET Composite Fiber Initiated by $\gamma$-Irradiation Postprint

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## Abstract

Reversible addition-fragmentation chain transfer (RAFT) mediated grafting of acrylonitrile onto Polyethylene/Poly(ethylene terephthalate) (PE/PET) composite fibers was performed using $\gamma$-irradiation as the initial source at ambient temperature. Different initial concentrations of 2-cyanoprop-2-yl dithiobenzonate were used as the chain transfer agent. The kinetics of graft polymerization is in accordance with the living RAFT polymerization. The successful grafting of acrylonitrile is proved by Fourier transform infrared spectroscopy analysis. The results of monofilament tensile test show that mechanical properties of the fibers change slightly after grafting. Scanning electronic microscopy images of the fibers show that the surface of RAFT grafted fibers is smoother than that of fibers grafted conventionally.

## Full Text

## Preamble

### Reversible addition-fragmentation chain transfer graft polymerization of acrylonitrile onto PE/PET composite fiber initiated by $\gamma$-irradiation∗

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**Abstract:** Reversible addition-fragmentation chain transfer (RAFT) mediated grafting of acrylonitrile onto Polyethylene/Poly(ethylene terephthalate) (PE/PET) composite fibers was performed using $\gamma$-irradiation as the initiation source at ambient temperature. Different initial concentrations of 2-cyanoprop-2-yl dithiobenzonate were used as the chain transfer agent. The kinetics of graft polymerization follows living RAFT polymerization behavior. Successful grafting of acrylonitrile is confirmed by Fourier transform infrared spectroscopy analysis. Monofilament tensile test results show that mechanical properties of the fibers change slightly after grafting. Scanning electron microscopy images reveal that the surface of RAFT-grafted fibers is smoother than that of fibers grafted conventionally.

**Keywords:** Radiation, Graft polymerization, Reversible addition-fragmentation chain transfer, Acrylonitrile, PE/PET composite fiber
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## Introduction

Surface modification of polymers is an important method for obtaining new materials from existing polymers with desirable bulk properties such as elasticity, permeability, and biocompatibility [1]. Graft polymerization [2–5] can be initiated by chemical initiators [4, 6], plasma treatment [7], and ionizing radiations [3, 8, 9]. Radiation-induced graft polymerization offers the advantage of avoiding chemical initiators, as ionizing radiations generate free radicals on various polymers at ambient temperatures to initiate graft polymerization [10, 11]. However, traditional radiation-induced graft polymerization does not provide controlled grafting kinetics, and both molecular weight and surface morphology of the product are uncontrollable.

Controlled/living radical polymerization, including nitroxide-mediated polymerization (NMP) [12, 13], atom transfer radical polymerization (ATRP) [14-16], and reversible addition-fragmentation chain transfer (RAFT) [17-19] polymerization, has developed significantly during the past two decades. NMP is not suitable for acrylonitrile (AN) due to its high reaction temperature [12], and ATRP cannot be initiated directly by $\gamma$-irradiation [16]. However, using the RAFT technique to graft polymers onto existing polymer matrices initiated by $\gamma$-irradiation at ambient temperature has been reported [1, 20, 21]. In RAFT polymerization, thiocarbonylthio compounds are used as chain transfer agents (CTA) to mediate polymerization and establish an equilibrium where all propagating chains have approximately the same chain length at any given time, making the polymerization controllable. This technique has been successfully applied to synthesize well-controlled brushes from polymer surfaces to obtain desirable surface properties for various materials.

Polyacrylonitrile (PAN) is a common polymeric material, and acrylonitrile is widely used in surface graft modifications of polymers because its reactive nitrile groups can be further derived into other useful groups such as amidoxime groups [22]. Polymerization of acrylonitrile via RAFT technique has been studied using 2-cyanoethyl dithiobenzoate (CED) [23], cumyl phenyldithioacetate (CPDA) [24], and 2-cyanoprop-2-yl dithiobenzonate (CPDB) [25]. In this paper, RAFT-mediated graft polymerization of acrylonitrile induced by $\gamma$-irradiation is investigated. Polyethylene/Poly(ethylene terephthalate) (PE/PET) composite fibers are used as the matrix material because the inner PET core is stable under irradiation while the outer PE layer readily generates free radicals upon $\gamma$-irradiation. 60Co $\gamma$-rays are used as the initiation source and CPDB as the CTA to graft AN onto PE/PET composite fibers, synthesizing PE/PET-g-PAN fibers with controllable degrees of grafting (DG) and desirable surface morphology. The kinetics of graft polymerization and characterization of chemical structure, thermal properties, and mechanical properties are presented. Scanning electron microscopy (SEM) is used to examine the surface morphology of the grafted fibers.

## II. Experimental

### A. Materials

PE/PET composite fibers were purchased from SINOPEC Shanghai Petrochemical Company. Dimethylformamide (DMF), AN, CPDB, and other chemical agents, all of analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd.

### B. RAFT Graft Polymerization

Monomer solutions of 5%-20% were prepared by dissolving acrylonitrile in DMF. Different amounts of chain transfer agent CPDB were added to the solutions, and the mixtures were contained in glass vials. PE/PET fibers were added to the vials and deoxygenated by bubbling with nitrogen gas for 15 min. The samples were irradiated at room temperature in a 60Co source to different doses at a dose rate of 0.18 kGy/h or to 12 kGy at different dose rates of 0.12, 0.16, 0.19, 0.23, and 0.3 kGy/h. Different initial monomer concentrations and initial molar ratios between monomer and RAFT agent ([AN]0/[CPDB]0) were used. For comparison, a group of samples without CPDB were irradiated to complete grafting polymerization. The grafted samples were extracted with DMF to remove homopolymer and vacuum-dried for 24 h.

### C. Degree of Grafting (DG)

The degree of grafting was calculated using the formula: $DG = [(Wg - W0)/W0] \times 100\%$, where Wg is the dry weight of grafted polymer and W0 is the initial weight of PE/PET fibers.

### D. Characterizations

A RAFT-mediated grafting polymer was measured on a gel permeation chromatography (GPC) system to analyze molecular weight and polydispersity index (PDI). The grafted polymers were characterized by FT-IR spectra on a Nicolet Avatar FT-IR spectrometer in the range of 3500-500 cm−1. Thermogravimetric (TG) analysis was performed on a TG 209 F3 Tarsus (NETZSCH, Germany) instrument at a heating rate of 10 °C/min under nitrogen atmosphere. Morphology and diameter of the fibers were analyzed with a scanning electron microscope (SEM) instrument (FESEM, JEOL, JSM6700F). Mechanical properties were tested on an Electronic Single Silk Strength Tester (LaiZhou Electron Instrument Co., Ltd.).

## III. Results and Discussions

### A. Kinetics of Graft Polymerization

The relationships between DG and absorbed dose, dose rate, monomer concentration, and CTA concentration were investigated. The dose-DG effect for PE/PET-g-PAN is shown in Fig. 1 [FIGURE:1], which presents DG versus absorbed dose at [AN]0/[CPDB]0 = 800:1 (a) and without CPDB (b), at a dose rate of 0.18 kGy/h and initial AN concentration of 15% (v/v). As shown in Fig. 1(a), for samples with an initial AN concentration of 15% (v/v) and [AN]0/[CPDB]0 = 800:1 irradiated to different doses at 0.18 kGy/h, DG increased linearly with absorbed dose. Free radicals that initiate graft polymerization were generated by $\gamma$-rays on the surface of PE/PET fibers and in the monomer solution. Propagating chains combined with the thiocarbonyl group of RAFT agents, which in turn released the living group radicals and re-initiated polymerization. All RAFT combining and releasing steps were reversible, and when equilibrium was established [26], the rate of free radical generation was proportional to the absorbed dose at a fixed dose rate. Since DG increase was proportional to the number of free radicals, DG increased linearly with dose when graft polymerization was performed in the presence of the RAFT agent (CPDB). However, without CPDB in the grafting system under the same conditions as the samples in Fig. 1(a), DG increase was not linear (Fig. 1(b)) because the equilibrium mentioned above did not exist.

The effect of dose rate on grafting rate is shown in Fig. 2 FIGURE:2 for 12 kGy-irradiated samples with an initial AN concentration of 15% (v/v) and [AN]0/[CPDB]0 = 800:1. As the rate of free radical generation is proportional to dose, the grafting rate (i.e., the amount of increased weight of PE/PET-g-PAN per hour) increased in a linear relationship with dose rate. Fig. 2(b) also shows a linear relationship between initial monomer concentration and DG for samples with [AN]0/[CPDB]0 = 800:1 irradiated to 12 kGy at 0.19 kGy/h.

The effect of RAFT agent concentration on DG was also studied, with initial molar ratios of [AN]0/[CPDB]0 ranging from 400:1 to 1500:1. As shown in Fig. 3 [FIGURE:3], DG changed only slightly. The radiation chemical yields

(G-values) of PE [27] and acrylonitrile [5] are 4 and 2.4–5.6 radicals per 100 eV, respectively. With AN concentration of 15% (v/v), assuming the weight of substrate polymer is 1 g, the number of free radicals generated by AN monomer and the substrate polymer is approximately 1.8 × 10^{16}. The minimum initial molar ratio between RAFT agent and monomer is 1:1500, so the number of CPDB molecules is approximately 2.8 × 10^{19}, far exceeding the number of free radicals. Therefore, when free radicals are generated, they combine immediately with RAFT agents to establish equilibrium, and grafting rates are approximately the same across this molar ratio range.

The kinetics results are in accordance with typical living polymerization, and the degree of grafting can be controlled by changing experimental conditions.

## B. Characterization of the PE/PET-g-PAN Fibers

**1. GPC Results** Since analyzing the molecular weight of grafting polymer in the composite fiber is difficult, the homopolymer in solution from the sample with DG = 4.2% (Fig. 1(a)) was measured by GPC. As shown in Fig. 4 [FIGURE:4], the polydispersity index of the homopolymer is 1.24, which is in agreement with results from conventional RAFT polymerization.

**2. FT-IR Spectra** Figure 5 [FIGURE:5] shows FT-IR spectra of pristine PE/PET composite fiber and PE/PET-g-PAN fibers with DG = 4.2% and 17%. The absorption bands at 2919 cm−1 and 2851 cm−1 are attributed to asymmetric and symmetric stretching of -CH2- groups, respectively [28]. Bending deformation of -CH2- groups is demonstrated by the absorption band at 1463 cm−1 [28]. The absorption bands at 1720, 1100, and 720 cm−1 represent stretching vibrations of ester groups, and para-substitution of benzene ring represented by the band at 870 cm−1 are attributed to PET fibers contained in the original composite fibers [29]. PAN graft chains are confirmed by nitrile groups in acrylonitrile, represented by the new peak at 2243 cm−1 in the spectra of grafted fibers [9]. The spectra also show that PE/PET-g-PAN with DG = 17% has a larger peak than that with DG = 4.2%. The FT-IR results indicate that acrylonitrile is successfully grafted onto PE/PET composite fibers.

**3. TGA Analysis** Thermal stability of pristine PE/PET fiber and grafted fibers was studied by TGA measurements. Fig. 6 [FIGURE:6] shows that PE/PET fiber began degrading at 336 °C, which is in accordance with the degradation temperature of PE. The residue should be attributed to the PET core of the fibers because PE gives no residue at 700 °C [29, 30]. From TG curves of the grafted fibers, two degradation stages are evident. The degradation stage at lower temperature is attributed to weak bonds formed on the pristine polymer by graft polymerization. The second degradation stage is due to grafted PAN chains [31], with its starting temperature decreasing as DG increases. The residue increased from 10.5% at DG = 4.2% to 17.1% at DG = 17.0%, which is due to carbonization of PAN grafted chains.

**4. Scanning Electron Microscopy** Surface morphology of RAFT-mediated grafted PE/PET-g-PAN fibers (DG = 10.0%) was compared with a PE/PET-g-PAN sample prepared via conventional graft polymerization (without CPDB) with a similar DG (10.3%). SEM images of the samples are shown in Fig. 7 [FIGURE:7]. The surface of RAFT-mediated PE/PET-g-PAN fibers was smoother than the conventional sample because RAFT-mediated polymerization is controllable through formation of intermediate radicals and the polymerization rate is steady, resulting in simultaneous growth of grafted chains with the same length at the same instant.

Figure 8 [FIGURE:8] shows SEM images of pristine PE/PET fibers and RAFT-mediated grafted fibers with DG = 17.0%. The diameters of pristine and grafted fibers are 17.27 µm and 19.72 µm, respectively. The fibers with DG of 17% still maintain a smooth surface. As mentioned above, RAFT-mediated graft polymerization was controlled by RAFT agent and the grafting rate was slow, so grafted chains propagated moderately without accumulating in one place.

**5. Mechanical Properties** Mechanical properties of PE/PET-g-PAN fibers, which are expected to be maintained to the maximal extent, are shown in Fig. 9 [FIGURE:9]. Breaking strength and breaking elongation of single fibers change only slightly compared to pristine PE/PET fibers because mechanical properties of the composite fibers are mostly attributed to the PET inner core, which is very stable under radiation [32].

## IV. Conclusion

Acrylonitrile has been successfully grafted onto PE/PET composite fibers via RAFT-agent-mediated free-radical polymerization initiated by $\gamma$-irradiation. The kinetics of graft polymerization indicate that the degree of grafting can be controlled by experimental conditions such as absorbed dose and initial monomer concentration. Successful grafting of PAN chains is confirmed by FT-IR measurements. Thermogravimetric analysis indicates that the degradation temperature of PAN graft chains is lower than that of pristine PE/PET chains and the residue increases with DG. SEM images show that RAFT-controlled grafted fibers have a smooth surface. Single fiber strength tests demonstrate that PAN grafting has little effect on the mechanical properties of the fibers.

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## Figures

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Figure 1: Figure 17