

Controlled Radical Polymerization of *N*-Vinylphthalimide Using Carboxyl-Terminated Trithiocarbonate as RAFT Agent and Preparation of Microfibers via Electrospinning Technique

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Received 10 November 2008; accepted 19 October 2009

DOI 10.1002/app.31619

Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Reversible addition-fragmentation chain transfer (RAFT) polymerization of *N*-vinylphthalimide in *N,N*-dimethylformamide (DMF) solution was carried out using 2-carboxypropan-2-yl dodecyl trithiocarbonate as a reversible chain transfer agent in the presence of 2,2'-azobisisobutyronitrile. The molecular weights of the polymers increased linearly with the monomer conversion and the molecular weight distributions were relatively narrow (PDI < 1.2). It is confirmed by chain extension reaction that the polymer prepared via RAFT polymerization can be used as a macro-RAFT agent. The structure of both polymers was characterized and confirmed by size-exclusion chromatogra-

phy and ¹H-NMR techniques. Ultrafine microfibers were prepared by electrospinning of poly(*N*-vinylphthalimide) in DMF solution. The effects of electrospinning process parameters such as voltage, tip-to-collector distance, and solution concentration on the morphology and the average size of the electrospun fibers were studied. To evaluate the fiber diameters, scanning electron microscope micrographs of the microfibers were performed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1005–1012, 2010

Key words: fibers; functionalization of polymers; living polymerization; polyimides; radical polymerization

INTRODUCTION

Free radical polymerization (FRP) is one of the most common synthetic methods for industrial preparation of polymers worldwide because of its high tolerance in relation to many monomer families and functional groups.¹ FRP has the major advantage that it is much less sensitive to traces of impurities than other types of polymerization, but the growing radical species formed during the stage of propagation usually suffer from chain transfer or bimolecular termination reactions such as recombination and disproportionation. This results in the formation of dead chains and end without control. As a result, the synthesis of well-defined architectures such as block copolymers, star polymers, and hyperbranched structures is not possible. Recent studies in the field of FRP aim to retain the advantages that FRP offers

while improving on its deficiencies. This has resulted in the development of new methods of polymer synthesis commonly referred to as “controlled/living radical polymerization.”^{2–5} A living polymerization implies the complete absence of chain transfer and chain termination.

The recent development of various controlled radical polymerization techniques has opened the way to the synthesis of polymer chains with well-defined structures and low polydispersities from a wider variety of monomers than in the case of ionic polymerization.^{6,7} The basic mechanism of control is based on establishing a rapid dynamic equilibration between a minor amount of growth-active radical species and a large majority of the dormant species, using some chemical species.^{8–10} A variety of strategies based on the common concept of alternating the activation and deactivation processes have been realized: Examples of reversible termination are atom transfer radical polymerization (ATRP)^{11–13} and nitroxide-mediated polymerization (NMP),^{14–18} whereas reversible addition-fragmentation chain transfer (RAFT)^{19–21} is an example of reversible transfer. Among the aforementioned techniques,

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RAFT is the most robust and versatile method, and is compatible with the broadest range of monomers and reaction conditions. In addition, the RAFT technique can be applied in emulsion and in miniemulsion polymerization.^{22,23}

In the RAFT process, a conventional radical initiator (2,2'-azobisisobutyronitrile, AIBN) is used with a functional chain transfer agents (CTAs) whose typical formula is $S=C(Z)SR$. The effectiveness of a CTA depends on the structures of the Z and R groups.¹⁹ Z is a group that governs the activity of the $C=S$ toward radical addition and R is a free radical leaving group that is capable of reinitiating polymerization. Generally, the RAFT agents that are used to mediate a RAFT polymerization are all based on the thiocarbonylthio species, such as dithioester,^{24,25} trithiocarbonate,^{26–28} xanthates, and some aromatic dithiocarbamates.^{29,30}

With appropriate choice of CTAs, a wide range of end-functional polymers and new varying architectures (gradient, block, tri- and multiarm, star and graft copolymers) of predetermined molecular weights and narrow polydispersity can be formed.

Interestingly, varieties of CTAs containing phthalimide groups were prepared and provide a route to end-functional polymers with predictable molecular weight and narrow molecular weight distributions.^{31–33} Postma et al.³⁴ reported that the RAFT polymerization of the less active monomers *N*-vinylpyrrolidone and vinyl acetate using *S*-phthalimidomethyl xanthates gave good control. After polymerization, reaction with hydrazine easily provides primary amine end-capped polymers by the cleavage of the phthalimide end-group.

This study focused first on the synthesis of poly(*N*-vinylphthalimide) (PNVPh), polymer of high T_g (201°C) and high-refractive index (1.620) potentially interesting for wave guide applications, by RAFT polymerization in dimethylformamide (DMF), using AIBN as initiator and 2-carboxypropan-2-yl dodecyl trithiocarbonate as chain transfer RAFT agent (CTA). We chose trithiocarbonate as the CTA agent for our studies based on its high efficiency of chain transfer, due to the tertiary carbon bearing a radical-stabilizing carboxyl group, attached to the labile sulfur atom.³⁵ To the best of our knowledge, the *N*-vinylphthalimide (NVPh) monomer has been long homopolymerized or copolymerized by FRP,^{36,37} but has not been polymerized via ATRP or NMP methods although it has been polymerized only one time by RAFT process.³⁸ In this article, an asymmetric trithiocarbonate-type RAFT agent bearing a carboxylic acid group at one end is reported.

Generally, the controlled/living polymerization of *N*-vinyl monomers with electron-donating group is difficult due to the less stabilization of the propagating radical during the growing process by the

unpaired electrons of the nitrogen, which acts as an electron donor group.^{37,38}

The second objective of our study was the preparation of nanofibers via the electrospinning process using the PNVPh prepared by RAFT technique in DMF solution. Electrospinning is among the most successful methods for producing nanofibers. This technology process, first patented by Formhals³⁹ in 1934, provides a simple and versatile method for generating ultrathin fibers from a wide variety of materials.^{40–45} The nanofibers can be used for various applications including filtration, drug delivery, solar cells, tissue engineering scaffolds, and nanotechnologies.⁴⁶

EXPERIMENTAL SECTION

Materials

The monomer NVPh (99%) was purchased from Aldrich and recrystallized from methanol before use. AIBN was twice purified by recrystallization from methanol, and stored in a refrigerator until needed. DMF was reagent grade and was used as received. All other reagents were of analytical grade and used as received.

Synthesis of RAFT agent

2-Carboxypropan-2-yl dodecyl trithiocarbonate was prepared according to the synthetic method described in Ref. 35. 1-Dodecanethiol (40.38 g, 0.20 mol), acetone (96.2 g, 1.655 mol), and tricaprylylmethylammonium chloride (3.245 g, 0.008 mol) were mixed in a flask cooled to 10°C under nitrogen atmosphere. Sodium hydroxide solution (50%) (16.77 g, 0.21 mol) was added over 20 min. The reaction was stirred for another 15 min before carbon disulfide (15.21 g, 0.20 mol) in acetone (20.18 g, 0.345 mol) was added over 20 min, during which time the color turned red. Ten minutes later, chloroform (35.625, 0.30 mol) was added in one portion, followed by dropwise addition of 50% sodium hydroxide solution (80 g, 1 mol) over 30 min. The reaction was stirred overnight. Three hundred milliliter of water was added, followed by 50 mL of concentrated HCl to acidify the aqueous solution. Nitrogen was bubbled through the reaction mass with vigorous stirring to help the evaporation of acetone. The solid was collected, and then stirred in 500 mL of 2-propanol. The undissolved solid was filtered off. The 2-propanol solution was concentrated to dryness, and the resulting solid was recrystallized from hexane to give a yellow crystalline solid.

¹H-NMR (in CDCl₃): 0.84 (t, 3H), 1.2–1.4 (m, 20H), 1.6–1.7 (s, 6H), 3.3 (t, 2H).

RAFT polymerization of N-vinylphthalimide

A general synthetic procedure is the following: a 50 mL polymerization tube equipped with a magnetic stirrer was charged with a mixture of NVPh (1.0 g, 5.8 mmol), CTA (12 mg, 3.3×10^{-2} mmol), AIBN (0.6 mg, 3.6×10^{-3} mmol), and 6 mL of DMF. The contents were purged with nitrogen to eliminate oxygen for ~ 30 min. The polymerization mixture was heated in an oil bath at 80°C for 8 h. For the kinetic measurements, samples of ~ 0.3 mL were withdrawn at various time intervals using an N_2 -purged syringe. Conversions and molecular weight of the samples were determined by $^1\text{H-NMR}$. The polymerization was stopped by air exposure and cooling. The final product was purified by precipitation into a large excess of methanol, filtered, and dried under vacuum at 50°C .

Polymerization of N-vinylphthalimide using PNVPh-SC(S)SC₁₂H₂₅ as macro-RAFT agent

The same procedure as for the RAFT polymerization of NVPh was used, except CTA was substituted by PNVPh-SC(S)SC₁₂H₂₅ obtained from the RAFT polymerization of NVPh.

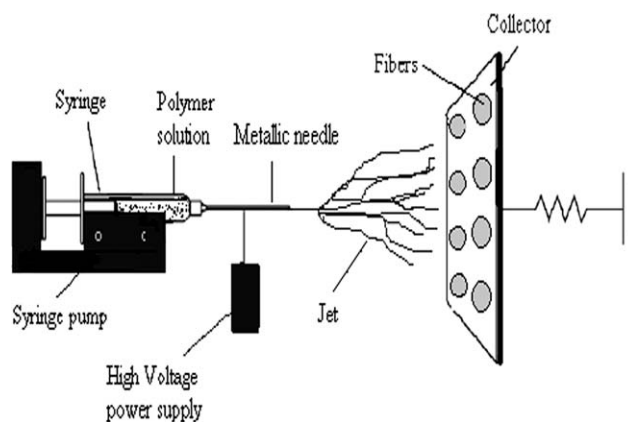
Electrospinning

Preparation of polymer solution

Three polymer solutions of poly(NVPh) with different concentrations ranging from 44 to 73 wt % are dissolved in DMF. The yellow solutions are stirred for several hours at room temperature. These solutions were electrospun at different voltages (15-20-30 kV) and needle tip-to-collector distances (6-10-16 cm) from a 1 mL syringe equipped with a 21 gauge needle.

Electrospinning process

The experimental apparatus used for electrospinning in this study is shown in Scheme 1. All experiments were conducted at room temperature. The solution for electrospinning was introduced in one-way plastic syringes attached to a flat-tipped steel needle and the syringes were placed horizontally on a syringe pump (Razel Scientific Instruments, Model A 99). A high voltage was applied between the needle and collector by means of a high-voltage power supply (Spellman SL10), the syringe pump was set at a flow rate of 0.762 mL h^{-1} for all experiments. The nanofibers were directly electrospun onto grounded aluminum scanning electron microscope (SEM) stubs covered with a sheet of aluminum foil, then sputtered with gold under vacuum and visualized by SEM.



Scheme 1 Used electrospinning setup.

Measurements

Molecular weights and polydispersity indices (PDI) of polymers were assessed by size-exclusion chromatography (SEC) using a Waters 610 system equipped with refractive index and ultraviolet detectors at 50°C . The system was operated at a flow rate of 1.0 mL min^{-1} using DMF containing 25 mM LiBr as an eluent. The columns were calibrated with polystyrene standards.

Spectroscopic characterization by $^1\text{H-NMR}$ was performed at room temperature with a Bruker 400 MHz instrument using CDCl_3 as solvent and tetramethylsilane (TMS) as internal reference.

SEM (Jeol JSM 840A) was used to study the morphology of the electrospun nanofibers.

RESULTS AND DISCUSSION

RAFT polymerization

The RAFT polymerization of NVPh was carried out using 2-carboxypropan-2-yl dodecyl trithiocarbonate as a CTA and AIBN as a conventional radical initiator at [CTA] : [AIBN] ratio of 10 : 1. For solubility reasons, DMF was selected as a suitable solvent in this polymerization. The initial monomer concentration was fixed at 1 mol L^{-1} and the amount of the RAFT agent was calculated so that the theoretical molecular weight at 100% conversion will be $30,000 \text{ g mol}^{-1}$. The experimental conditions and the results are summarized in Table I.

The theoretical molecular weights values, which were obtained using eq. (1), show good correlation with the experimentally determined molecular weights ($M_{n,\text{NMR}}$).

$$M_{n,\text{th}} = m_{\text{RAFT}} + \frac{[\text{M}]_0 \cdot m_{\text{M}} \cdot \text{conv.}}{[\text{RAFT}]_0} \quad (1)$$

where $[\text{M}]_0$ and $[\text{RAFT}]_0$ are the starting concentrations of the NVPh and the RAFT agent, conv. is the

TABLE I
Synthesis Parameters for the RAFT Polymerization of
***N*-Vinylphthalimide at 80°C, [NVPh]₀ : [RAFT] : [AIBN]**
= 175 : 1 : 0.1; [NVPh] = 1 mol L⁻¹

Run	<i>t</i> (min)	Conv. (%)	<i>M_{n,SEC}</i> ^a (g mol ⁻¹)	<i>M_{n,NMR}</i> ^b (g mol ⁻¹)	<i>M_{n,th}</i> ^c (g mol ⁻¹)	PDI
1	30	8	–	1500	2700	–
2	75	20	18000	4200	6400	1.10
3	165	27	25500	5500	8500	1.16
4	255	30	27100	6400	9400	1.16
5	375	33	27900	7500	10,300	1.16
6	465	36	28900	8000	11,300	1.14

^a Measured by SEC using DMF as eluent and polystyrene as calibration standards.

^b Measured by ¹H-NMR analysis using CDCl₃ as solvent and TMS as the internal standard.

^c Calculate according to $M_{n,th} = [M]_0/[RAFT]_0 \times \text{conv.} \times 173.17 + (\text{molecular weight of RAFT agent})$.

fractional conversion, and m_M and m_{RAFT} are the molecular weight of the monomer and RAFT agent.

As presented in Figure 1, the SEC chromatograms of the synthesized homopolymers were unimodal with narrow molar mass distribution, demonstrating the efficient polymerization control with the chosen RAFT agent. In accordance with the observations reported by Maki et al., a fast consumption of our CTA and resulting uniform initiation is expected since the chosen CTA should easily give a tertiary radical stabilized by the carboxylic group.

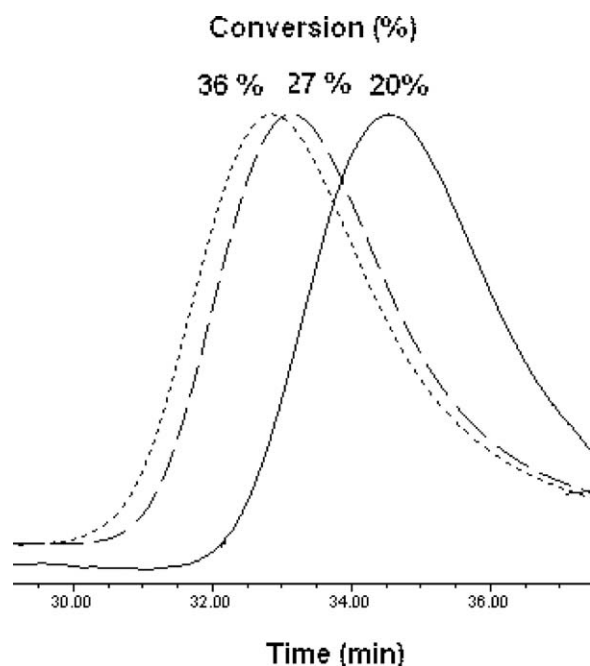


Figure 1 SEC traces of PNVPPh formed by polymerization of NVPh with AIBN as initiator and 2-carboxypropan-2-yl dodecyl trithiocarbonate as RAFT agent at 80°C.

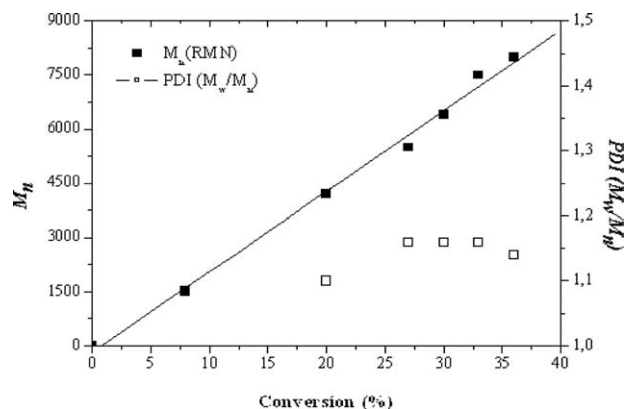


Figure 2 Dependence of number-average molecular weight M_n and polydispersity index PDI (M_w/M_n) on the conversion for the RAFT polymerization of NVPh at 80°C in DMF. Polymerization conditions: [NVPh]₀ : [RAFT] : [AIBN] = 1750 : 10 : 1.

The dependence of the number average molecular weights and PDI of the polymers on the monomer conversion is shown in Figure 2. The number-average molecular weights increased linearly with conversion, implying a constant number of growing chains during the polymerization and demonstrating the excellent reproducibility of the RAFT polymerization of NVPh with CTA. The polydispersity of the resulting PNVPPh was constantly low, with values from 1.10 to 1.16 (see Table I), indicating that the polymerization was under control.

The kinetic plot for RAFT polymerization of NVPh is shown in Figure 3. The corresponding plot of $\ln(1/(1-C))$ versus time was linear and nearly first-order kinetic with molar ratio of [NVPh]₀ : [RAFT] : [AIBN] = 1750 : 10 : 1. The curve was linear during the first hour of polymerization meaning the absence of termination reaction. After 2.5 h of polymerization time, the polymerization rate decreased and the observed curve indicate that

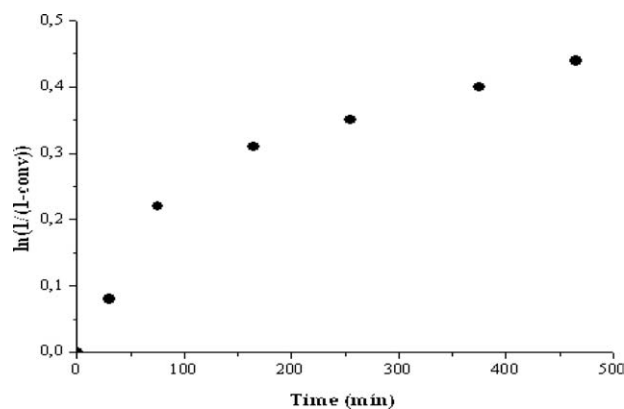


Figure 3 Kinetic plots for RAFT polymerization of NVPh in DMF solution at 80°C. Polymerization conditions: [NVPh]₀ : [RAFT] : [AIBN] = 1750 : 10 : 1, [NVPh]₀ = 1 mol L⁻¹.

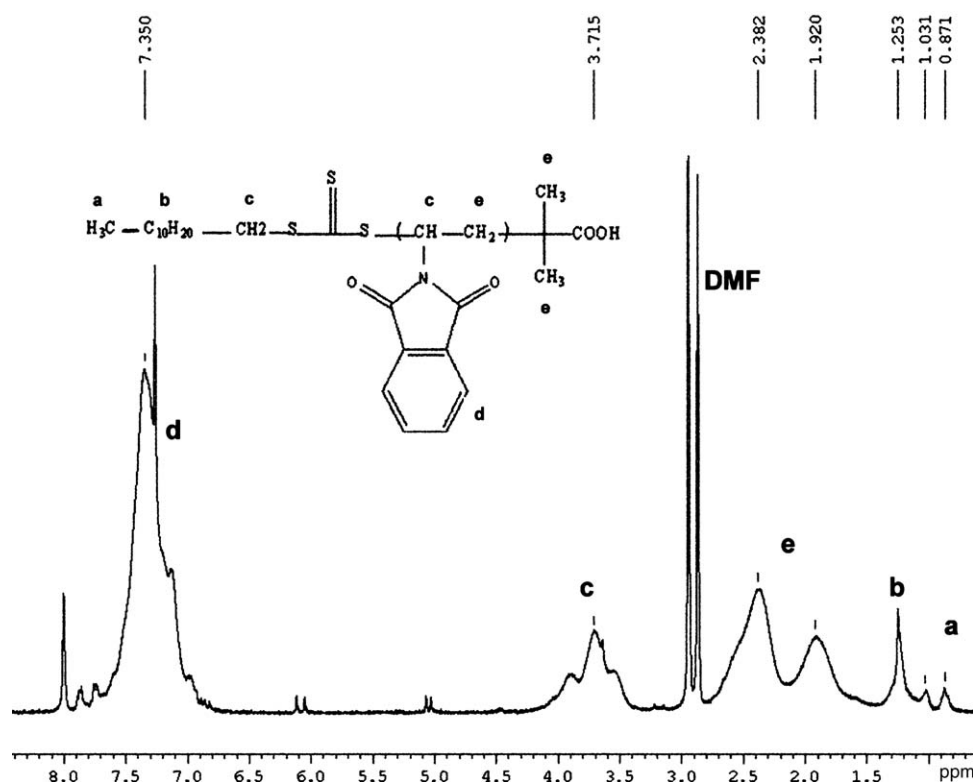


Figure 4 $^1\text{H-NMR}$ spectrum of PNVPh ($M_{n,SEC} = 27,100$, PDI = 1.16) polymer using CDCl_3 as solvent and TMS as the internal standard.

generation of active radicals by dormant species did no longer balance the loss by irreversible termination reactions of the propagating species. Some unfavorable termination reactions at the initial stage could be due to the quite high temperature used for the polymerization (80°C), which may lead to the decreased selectivity of the various radical reactions to promote unfavorable side and/or termination reactions. At this temperature, it is also possible that AIBN is fully decomposed after a few hours, resulting in the formation of a dead-end polymer at the initial stage of polymerization. This might be improved by decreasing the polymerization temperature.

From all the obtained results, we may conclude that an excellent degree of control is achievable with the RAFT process of NVPh using 2-carboxypropan-2-yl dodecyl trithiocarbonate as CTA. However, a pseudo-first-order kinetic with a long-time induction period for the same monomer using other CTA was reported recently.³⁸

To confirm the polymer structure and to know information on polymer end groups, the $^1\text{H-NMR}$ spectra were examined; a typical spectrum is shown in Figure 4. Except the characteristic signals on PNVPh, we can find the signals at 3.5–4.1 ppm corresponding to the methylene protons of CTA and methine proton of PNVPh. The signals at $\delta = 0.84$ ppm attributed to the methyl protons of CTA, con-

firm that the RAFT agent moiety remained at the end of the polymer chains. The $M_{n(NMR)}$ listed in Table I was calculated according to eq. (2):

$$M_{n(NMR)} = (3xI_p)/I_a x 173.17 + 364 \quad (2)$$

where I_p and I_a are the integral values of methine proton of PNVPh (integral value of the methylene proton of CTA was considered negligible compared with the integral value of methine proton of PNVPh) and methyl protons of CTA, respectively. 173.17 and 364 are respectively the molecular weights of NVPh and CTA.

The polymers obtained from the RAFT polymerization of NVPh have the moiety trithiocarbonate at the end, which could be used in a chain extended. The PNVPh ($M_{n,SEC} = 47,700 \text{ g mol}^{-1}$, PDI = 1.34) as macro-RAFT agent was added to a solution of NVPh monomer and AIBN as initiator at 80°C for the synthesis of chain-extended polymers. The polymerization was carried out with a molar ratio CTA/AIBN of 10, to ensure a good control of the polymerization. The analysis of the obtained polymer by SEC (Fig. 5), shows that the molecular weight was shifted toward higher molecular weight ($M_{n,SEC} = 62,000 \text{ g mol}^{-1}$) after 5 h of reaction. On the other hand, the PDI of the chain extension product varying from 1.34 to 1.4 is a little higher than the PDI of the original polymer. This may be caused by the fact

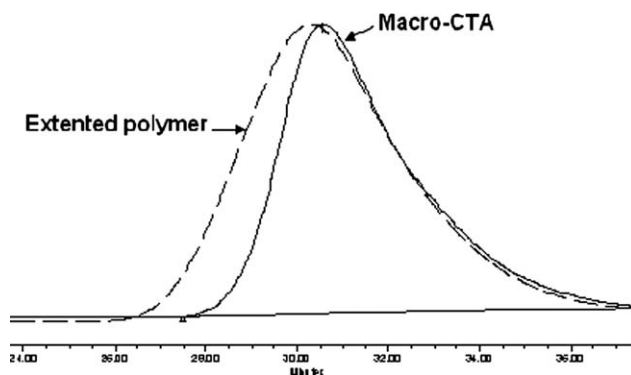


Figure 5 SEC curves before and after chain extension reaction using PNVPPh samples as macro-RAFT agents. PNVPPh, $M_{n,SEC} = 47,700 \text{ g mol}^{-1}$, PDI = 1.34 (solid traces). Chain-extended PNVPPh, $M_{n,SEC} = 62,000 \text{ g mol}^{-1}$, PDI = 1.41 (dotted traces).

that the chain extension was carried out with polymer obtained with a high conversion (82%) or by a possible free homopolymerization of NVPh initiated by AIBN, which occurs simultaneously. However, these results suggest that most ends of the chains of the poly(NVPh-CTA) may be functionalized with tri-thiocarbonate end groups and should give block copolymers by reinitiating in the presence of other monomers.

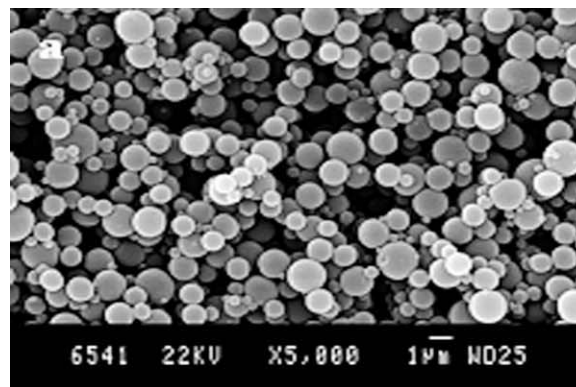
Electrospinning of PNVPPh

The as-obtained PNVPPh was then used to prepare microfibers by using the electrospinning process. To study the influence of polymer concentration on the electrospinning process, three polymer solutions with various concentration: 44 wt %, 60 wt %, and 73 wt % were electrospun under the same conditions (at a voltage of 20 kV, needle tip-to-collector distance of 15 cm and flow rate of 0.762 mL h^{-1}). Figure 6 shows SEM photographs of the electrospun PNVPPh. Microspheres could be seen on the electrospun material prepared from the polymer with 44 wt % [Fig. 6(a)]. As the concentration of the solution polymer increased from 44 wt % to 60 wt %, mixtures of microspheres and short broken fibers were obtained [Fig. 6(b)]. For PNVPPh at 73 wt % [Fig. 6(c)], uniform, straight, and smooth microfibers were observed, indicating that this concentration is very good for producing fibers. The morphology of the electrospun fibers was greatly influenced by the concentration of the polymer solution, the highest concentration allowing the production of uniform fibers with diameters in the micrometer range. It has also to be mentioned that a $M_{n,SEC}$ of $39,000 \text{ g mol}^{-1}$ for PNVPPh is high enough to get homogeneous fibers.

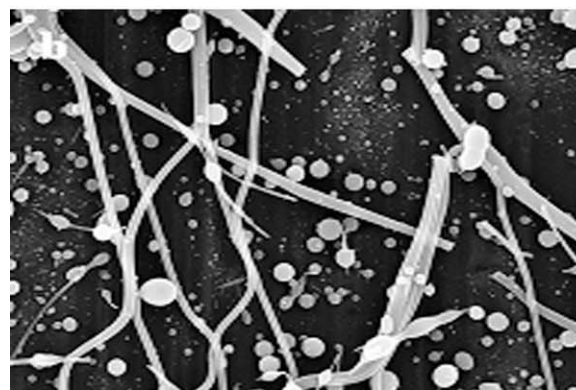
Further, the effects of the voltage and the needle tip-to-collector distance on the morphology of electrospun PNVPPh were also investigated. The SEM

images of fibers electrospun at 73 wt %, with varying voltage and needle tip-to-collector distance is shown in Figure 7.

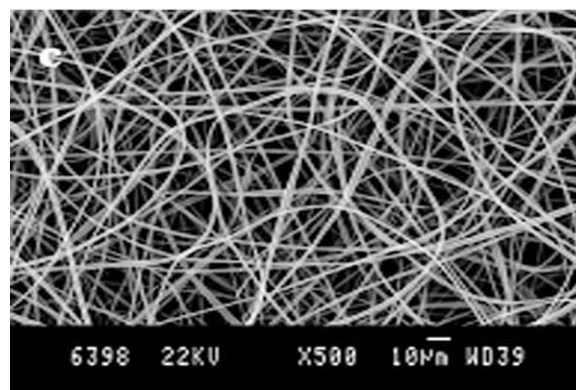
In Figure 7(a), the diameter of the fibers obtained at 15 kV and 15 cm tip-to-collector distance ranged from 1.4 to 1.7 μm . When the voltage increase to 20 kV [Fig. 7(b)] one obtained even thinner fibers, down to 1 μm ; nevertheless, the mean diameter of the fibers remained in the range 1.4–1.6 μm , and the



(a)



(b)



(c)

Figure 6 SEM photographs of electrospun poly(*N*-vinylphthalimide) as function of solution concentration at voltage of 20 kV and needle tip-to-collector distance of 15 cm: (a) 44 wt %, (b) 60 wt %, and (c) 73 wt %.

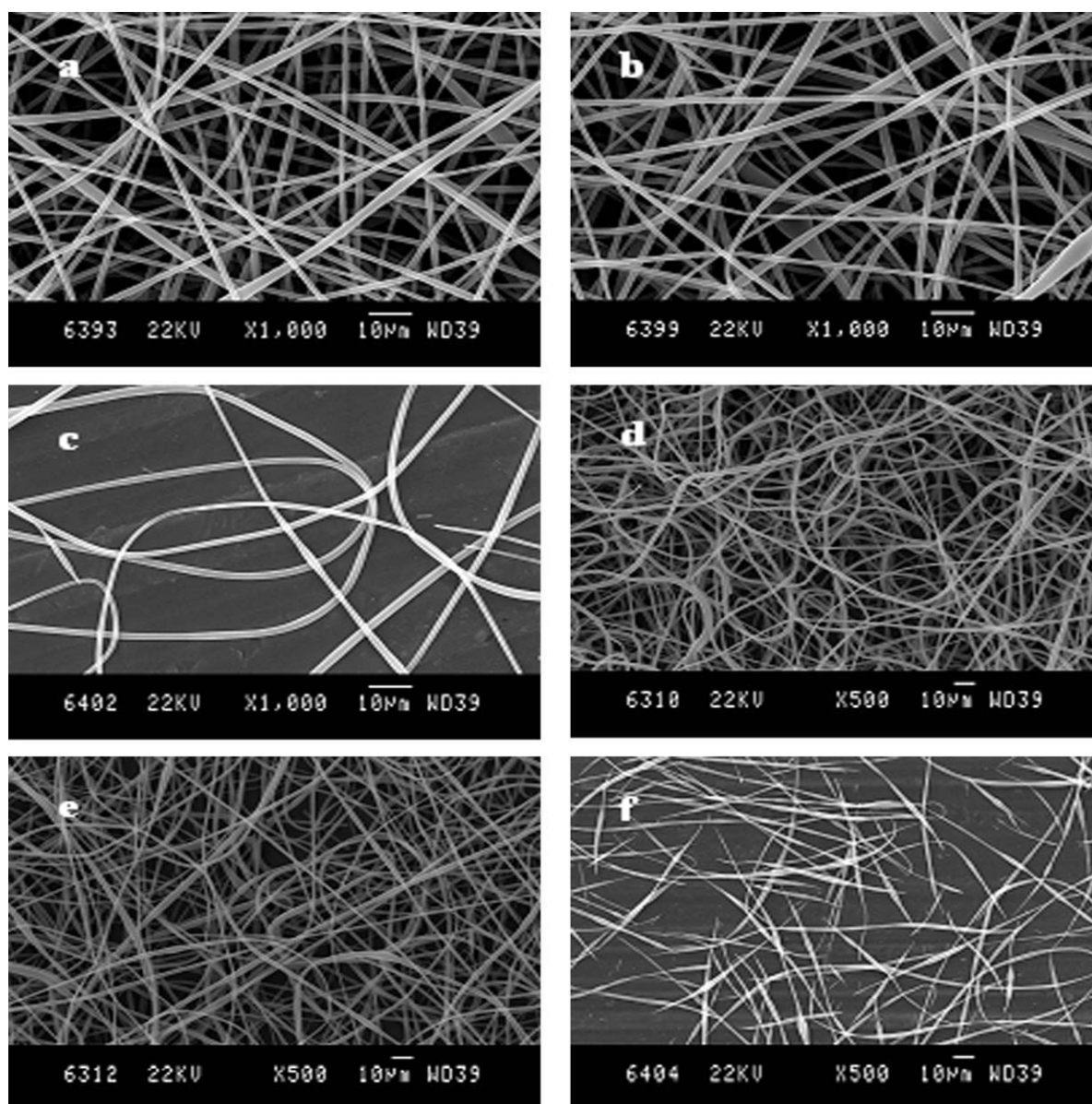


Figure 7 SEM photographs of electrospun poly(*N*-vinylphthalimide) fibers from a 73 wt % solution in DMF as functions of: the voltage: (a) 15 kV, (b) 20 kV, (c) 30 kV and of the needle tip-to-collector distance: (d) 6 cm, (e) 10 cm, (f) 16 cm.

maximum diameter around 2.2 μm . When the voltage was enhanced to 30 kV, the production of broken fibers occurs, with however a really narrow diameter distribution: 1.2–1.8 μm [Fig. 7(c)]. As for the influence of electrospinning voltage, we found that the fiber morphology changed and the fiber diameter decreased with the increasing of needle tip-to-collector distance [Fig. 7(d–f)]. In the case presented in Figure 7(f), broken and spindle-shaped fiber fragments with diameters varying between 0.5 and 4.5 μm were formed. In comparison with the sample shown in Figure 7(b), the only difference in the electrospinning setup consisted of 15 versus 16 cm distance between needle and collector. This result indicated that over a certain tip-to-collector distance was

not possible to form continuous fibers, probably related to different reasons: The instability of the jet of polymer solution, surface tension of the polymer solution, or nature of the solvent used. This aspect will be more studied in a future work.

CONCLUSIONS

This work evidenced that the RAFT polymerization of NVPh is controlled by using a trithiocarbonate-type CTA, i.e., 2-carboxypropan-2-yl dodecyl trithiocarbonate. Suitable molar ratios for the control have been found to be $[\text{NVPh}]_0 : [\text{RAFT}] : [\text{AIBN}] = 1750 : 10 : 1$. The molecular weights and molecular weight

distributions of the obtained polymers indicated a linear increase of M_n with conversion and PDIs between 1.10 and 1.16, confirming that the reaction undergoes a controlled mechanism. The kinetic investigation showed that the RAFT process of NVPh proceeded in a living way. The use of this CTA provides thus asymmetric end-capping of PNVPh with a carboxylic acid at one chain-end.

This synthesized functional PNVPh has then been processed as fibers by electrospinning. The minimum concentration has been determined to reach fibers rather than microspheres. Polymer solution (73 wt %) in DMF favors the formation of uniform, straight, and smooth fibers of about 1 μm diameter. SEM observations showed that the diameter of the nanofibers increased with increasing concentration of the solution and decreased slightly with increasing the voltage and needle tip-to-collector distance.

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