Research Article

Nitroxide-mediated copolymerization of styrene and pentafluorostyrene initiated by polymeric linoleic acid

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Polymeric linoleic asit graft copolymers were synthesized via a nitroxide-mediated radical polymerization (NMRP) method in the presence of 2,2-6,6-tetramethylpiperidinyl-1-oxy (TEMPO). For this purpose, PLina-ox was exposed to polymerization with styrene (Sty) or Sty and pentafluorostyrene (F_5Sty) in the presence of TEMPO by NMRP method in order to obtain PLina-g-PSty and PLina-g-PF_5Sty-g-PSty graft copolymers with controlled structure and low polydispersity. Chain extension study was evaluated. Principal parameters, such as monomer concentration, initiator concentration, and polymerization time, which effect the polymerization reactions, were evaluated. The products thus obtained were well characterized by ^{1}H NMR, GPC, and ^{19}F NMR measurements.

Practical application: We report for the first time the synthesis of PLina-*g*-PSty and PLina-*g*-PSty-*g*-PF_5Sty graft copolymers in the presence of TEMPO. NMRP reactions were performed in the presence of TEMPO in order to obtain graft copolymers with controlled molecular weight and polydispersity. Chain-extension reactions were also successfully carried out because of the activation of TEMPO terminated chain ends of graft copolymers. Pure linoleic acid was auto-oxidized under daylight and air oxygen, yielding peroxidized PLina (PLina-ox). PLina-ox has been used in the polymerization of styrene (Sty) or copolymerization of Sty and pentafluorostyrene (F_5Sty).

Keywords: Autoxidation / Linoleic acid / Nitroxide-mediated radical polymerization / Pentafluorostyrene

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1 Introduction

Nitroxide-mediated radical polymerization (NMRP) [1, 2] is one of the most attractive controlled radical polymerization techniques such as single-electron transfer-mediated living radical polymerization (SET-LRP) [5, 6], reversible addition–fragmentation chain transfer polymerization (RAFT) [7–10], and atom transfer radical polymerization (ATRP) [11–14]. In the last two decades, these techniques have been widely used to synthesize polymers with controlled topologies and very low polydispersity indices (PDI). In particular, NMRP has several advantages over SET-LRP, ATRP, and RAFT polymerization with the most important one being that NMRP does not require the use of metal salts or sulfur compounds [15]. Therefore, there is no extensive purification step required and the obtained well defined polymers can be used in biological applications [16].

NMRP can be carried out simply by using a free radical initiator and a stable free nitroxide. Firstly, initiation takes place rapidly when the reaction is conducted at temperatures higher than 90°C. Thus, all polymer chains would be initiated simultaneously at the early stages of the polymerization. Secondly, the initiated polymer chains are reversibly capped by a stable-free radical, such as 2,2-6,6-tetramethylpiperidinyl-1-oxy (TEMPO), to provide a dormant living polymer. Reversible activation deactivation of the chain end provides control over the polymerization of monomers, such as styrene [17].

To synthesize oil-based polymers, one of the most general route is auto-oxidation of polyunsaturated oil/oily acids.

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Abbreviations: ATRP, atom transfer radical polymerization; M_n, molecular weight; **NMRP,** nitroxide-mediated radical polymerization; **F_5Sty,** pentafluorostyrene; **PLina-ox,** peroxidized PLina; **RAFT,** reversible addition–fragmentation chain transfer polymerization; **SET-LRP,** single-electron transfer-mediated living radical polymerization; **Sty,** styrene; **TEMPO,** 2,2-6,6-tetramethylpiperidinyl-1-oxy

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Hydroperoxidation, peroxidation, epoxidation, and perepoxidation reactions were performed under ambient conditions in the presence of oxygen and daylight. Using this method, polyunsaturated oil/oily acids are utilized to obtain macroperoxy initiators and graft copolymers were obtained via free radical polymerization [18–23]. We have previously reported several studies to obtain styrene graft copolymers using polymeric linoleic acid. Çakmaklı et al. reported polymeric linoleic acid (PLina) initiated free radical polymerization of styrene to obtain PLina-g-PSty graft copolymers [24]. These copolymers contain different polymeric oily acid initiators and they have investigated the relationship between the polymer structures and dynamic mechanical properties [25]. Allı et al. reported one-pot synthesis of poly [(linoleic acid)-*g*-(styrene)-*g*-(ϵ-caprolactone)] graft copolymers by ring opening polymerization and free-radical polymerization in one pot [26]. These copolymers have been investigated regarding their enzymatic degradation properties in the presence of Pseudomonas lipase [27].

NMRP has not been widely utilized in connection with polymeric fatty oil copolymerizations. To date, there are only a couple of reports describing the styrenation of air-blown linseed oil [28] and styrenation of triglyceride oil [29]. To the best of our knowledge, there are no reports on the comparison of free radical polymerization and NMRP on the preparation of unsaturated fatty acid grafted copolymers and their chain extension reactions. In this study, we report for the first time the synthesis of PLina-*g*-PSty and PLina-*g*-PSty-*g*-PF_5Sty graft copolymers and their chain extension. Pure linoleic acid was auto-oxidized under daylight and air oxygen, yielding peroxidized PLina (PLina-ox). PLina-ox has been used in the polymerization of styrene (Sty) or copolymerization of Sty and pentafluorostyrene (F_5Sty). NMRP reactions were performed in the presence of TEMPO in order to obtain PLina-*g*-PSty and PLina-*g*- PF_5Sty-*g*-PSty graft copolymers with controlled molecular weight and polydispersity. Chain-extension reactions were also successfully carried out because of the activation of TEMPO-terminated chain ends of graft copolymers. Relatively high molecular weights have been achieved.

2 Materials and methods

2.1 Chemicals

Linoleic acid (*cis-cis*-9-12-octadecadienoic acid) was supplied from Fluka (Steinheim, Germany), and used as received. Sty and F_5Sty were supplied by Aldrich, which was purified extensively by washing with 10 wt% aqueous NaOH solution, drying over anhydrous $CaCl_2$ overnight, and distilling over CaH_2 under reduced pressure prior to use. All other chemicals were of analytical grade and used without further purification. PLina-ox was obtained through autoxidation of linoleic acid as previously reported [24, 30]. Linoleic acid thickness in Petri dish (ca. 2.0 mm) and the time of exposition of the oil layer to air oxygen were the variances of the autoxidation procedure. 10.0 g of linoleic acid spread out in a Petri dish ($\varphi = 5$ cm) was exposed to daylight in the air at room temperature. A pale-yellow viscous liquid polymeric linoleic acid peroxide was obtained after 2 months autoxidation. Autoxidation of linoleic acid was stopped when it was transferred into the bottle with a lid to keep at room temperature. ^{1}H NMR spectrum of PLina-ox contained characteristic peaks of the related groups: (ô, ppm): 5.6–6.3 ppm (the vinyl protons of the fatty acid macroperoxides), 2.3 ppm (–CH_2–COOH of fatty acid macroperoxide). Peroxide analysis of the PLina-ox fraction was carried out by a reflux of a mixture of 2-propanol (50 mL)/acetic acid (10 mL)/saturated aqueous solution of KI (1 mL) and 0.1 g of PLina-ox for 10 min and titrating the released iodine against thiosulfate solution, according to a literature procedure [31]. The peroxygen content of the PLina-ox sample was found to be approximately 0.9.

2.2 Instrumentation

The ^{1}H NMR and ^{19}F NMR spectra of the polymers were recorded on a Bruker AVANCE 400 spectrometer (400 MHz), using $CDCl_3$ as a solvent. SEC measurements were performed using PL50 system equipped with a UV (254 nm) and a RI detector. Calibration was carried out using polystyrene standards provided by Polymer Laboratories. Seven polymer standards with various molar mass were used, 1260, 4920, 9920, 30300, 60450, 170 800, and 299 400 Da. Tetrahydrofuran (THF) was used as an eluent at 40°C at a flow rate of 1 mL/min.

2.3 Synthesis of PLina-*g*-PSty graft copolymers using TEMPO

The typical polymerization procedure was as follows: 0.50 g of PLina-ox and required amount of TEMPO were charged into a flame-dried Schlenk flask, fitted with a magnetic stirring bar. Then 2.78 g of styrene and 3 mL anisole as solvent were injected into a Schlenk flask by a syringe under argon atmosphere. The flask was placed into a preheated oil bath at 130°C. Other conditions are shown as follows: the feed ratio was [PLina-ox]:[TEMPO]:[Sty] = [1]:[1]:[100] and the reaction time was chosen as 4, 9, and 20 h. After the polymerization, the crude polymer was dissolved in chloroform and precipitated into excess of methanol. Finally, precipitated polymer was dried under vacuum at 40°C for 24 h.

2.4 Synthesis of PLina-*g*-PF_5Sty-*g*-PSty graft copolymers using TEMPO

The typical polymerization procedure was as follows: 0.50 g of PLina-ox and required amount of TEMPO were charged into a flame-dried Schlenk flask, fitted with a magnetic

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stirring bar. Then 1.51 g of styrene, 1.8 g pentafluorostyrene, and 6.30 mL anisole as solvent were injected into the Schlenk flask by a syringe under argon atmosphere. The flask was placed into a preheated oil bath at 130°C. Other conditions are shown as follows: the feed ratio was [PLina-ox]:[TEMPO]:[Sty]:[F_5Sty] = [1]:[1]:[50]:[50] and the reaction time was chosen as 4, 8, 10, 20, 25, and 30 h. After the polymerization, the crude polymer was dissolved in chloroform and precipitated into excess of methanol. Finally, precipitated polymer was dried under vacuum at 40°C for 24 h.

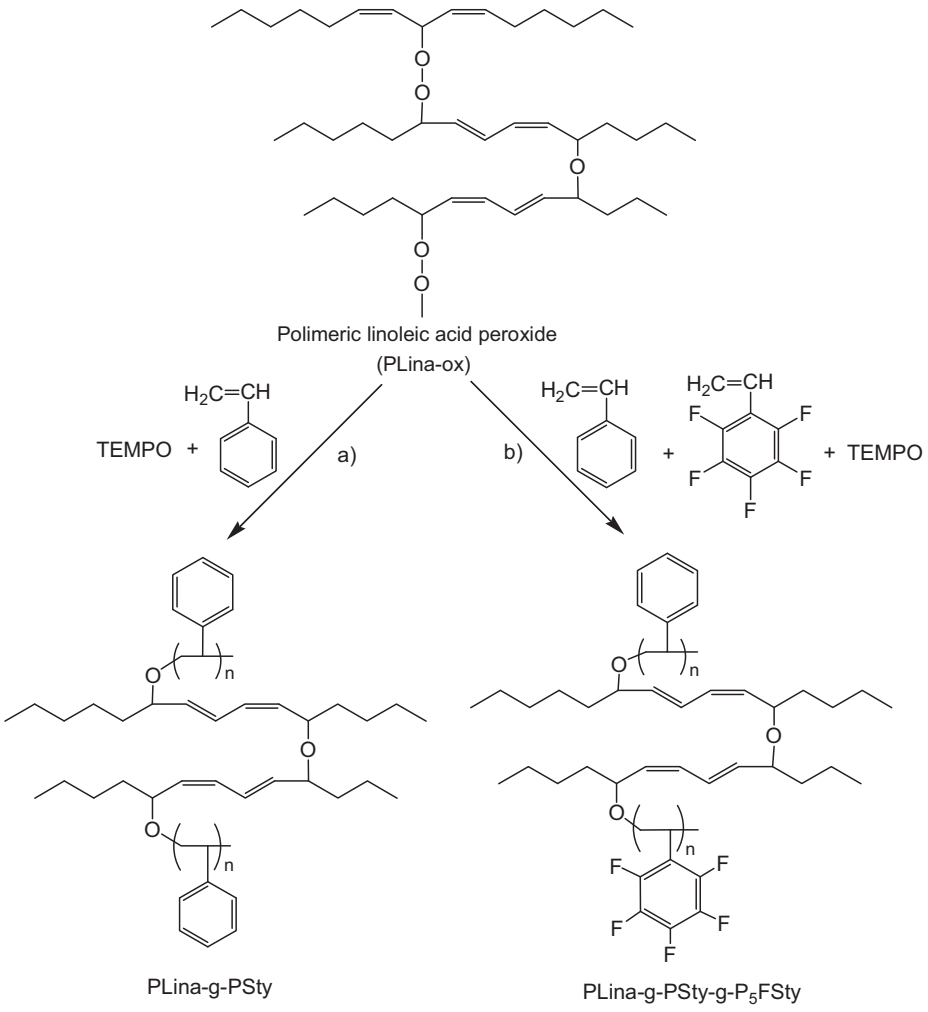
2.5 Chain extension of PLina-*g*-PSty graft copolymers with styrene

The typical polymerization procedure was as follows: 0.50 g of PLina-g-PSt was charged into a flame-dried Schlenk flask fitted with a magnetic stirring bar. Then 1.73 g of styrene and 1.9 mL anisole as solvent was injected into the Schlenk flask by a syringe under argon atmosphere. The flask was placed into a preheated oil bath at 130°C. Chain extension reaction was carried out at various reaction times, such as 4, 8, 10, 20, and 25 h. The crude polymer was dissolved in chloroform and precipitated into excess of methanol. Finally, precipitated polymer was dried under vacuum at 40°C for 24 h.

3 Results and discussion

3.1 Synthesis of the macroperoxy initiator from linoleic acid

We have recently demonstrated the use of PLina-ox, macroperoxy initiator, in free radical polymerization of selected vinyl monomers [24, 30]. PLina-ox is valuable for incorporating hydrophobic and biodegradable oil sourced polymer into graft copolymer structures. PLina-ox has peroxide groups that can



Scheme 1. Reaction design of the polymerization of a) styrene or b) styrene and pentafluorostyrene initiated by the fatty acid macroperoxides in the presence of TEMPO.

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be used to initiate the free radical polymerization of vinyl monomers. In this study, PLina-ox has been used in nitroxide-mediated radical polymerization of styrene and pentafluorostyrene to prepare PLina-*g*-PSt and PLina-*g*-PF_5St-g-PSty graft copolymers. PLina-ox, macroperoxy initiator, was autoxidized for 60 days and the molar mass was measured as 1450 Da (PDI = 1.41). Peroxygen content of the PLina-ox was found to be 0.9 wt%. Autoxidized linoleic acid acted as the macroperoxidic initiator in the polymerization of styrene and pentafluorostyrene.

3.2 Nitroxide-mediated radical controlled graft copolymerization

PLina-ox has peroxide groups that initiated free radical polymerization of styrene and pentafluorostyrene. Polymerization of styrene and pentafluorostyrene was initiated by PLina-ox initiator in the presence TEMPO and controlled radical polymerization provided well-defined PLina-*g*-PSty and PLina-*g*-PF_5St-g-PSty graft copolymers. Scheme 1 shows the reaction design of Sty or Sty and F_5Sty polymerization initiated by macroperoxide, PLina-ox in the presence of TEMPO. This controlled graft copolymerization approach has been studied extensively by varying the polymerization time, Sty and F_5Sty concentration, chain extension as well as the PLina-ox macroperoxy initiator concentration. The obtained results are summarized in Tables 1–3. All obtained graft copolymers have been precipitated from $CHCl_3$ to methanol.

The effects of polymerization time on the graft copolymerization and homo polymerization by the application of controlled-free radical polymerization using TEMPO have been studied. Homo polymerization of styrene using TEMPO and nitroxide-mediated polymerization of styrene using PLina-ox and TEMPO have been carried out. The effects of the polymerization time on the graft and homo polymerization are presented in Table 1. Polymerization reaction is carried out at various times such as 4, 9, and 20 h.

Table 1. Reaction conditions and characterization of PLina-g-PSty and homo polystyrene

Run No.[a]	Time (h)	PSty (%)[b]	$M_{n,GPC}$	$M_{w,GPC}$	*PDI*
PLinaSty-1	4	12.4	1460	1820	1.25
PLinaSty-2	9	24.4	5210	5770	1.11
PLinaSty-3	20	46.1	7420	9240	1.25
HSty-1	4	3.2	300	320	1.05
HSty-2	9	10.6	320	340	1.07
HSty-3	20	14.8	1110	1220	1.10

[a]All polymerization were carried out in 50% (v/v) anisole with PLina-ox:0.5 g, Sty:2.78 g, and [PLina-ox]:[TEMPO]:[Sty]:[1]:[1]:[100] at 130°C.
[b]Determined by ^{1}H NMR.

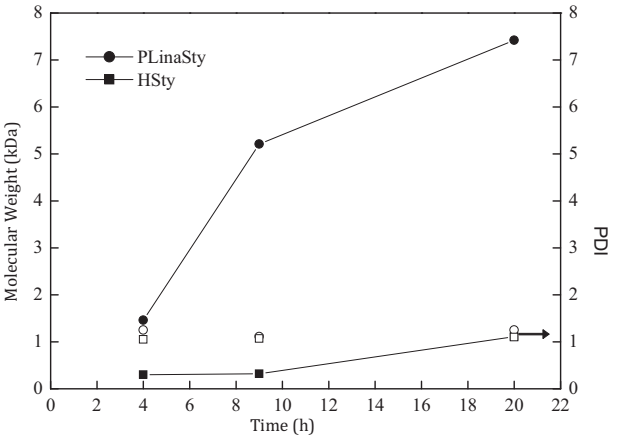

Figure 1. Variation of molecular weight (M_n) and polydispersity versus the polymerization time of PLina-g-PSty graft copolymer and homo polystyrene.

Weight percentages of each block in the structure of graft copolymers and homo polymers were determined from ^{1}H NMR. The amount of polystyrene in the graft copolymer has increased according to longer polymerization time. The percentages of the amount of PSty in graft copolymer is found to be 12.43% in PLinaSty-1, 24.35% in PLinaSty-2, and 46.11% in PLinaSty-3 while the percentages of the amount of PSty in homo polymer is found to be 3.17% in HSty-1, 10.58% in HSty-1, and 14.81% in HSty-1.

The plot of molecular weight (M_n) versus polymerization time is shown in Fig. 1. For polymerizations of longer periods, polymers of higher molecular weights are obtained. Longer polymerization times cause higher polymer yields. It can be said that graft copolymers were successfully synthesized using PLina-ox with TEMPO when we compare the molecular weights of graft copolymers and homo polymers. M_n of the PLina-*g*-PSty graft copolymers are changing between 1460 and 7420 Da while M_n of homo polymers are 300 and 1110 Da, respectively. Polymerization can also confirmed as a controlled polymerization when we take into account the low polydispersity indices, which are changing between 1.11 and 1.25.

The relationship between the monomer conversion and polymerization time has been shown in Fig. 2. It was found that the monomer conversion values have increased by extended reaction times as expected. The yield for PLina-*g*-PSty graft copolymer has been obtained as 13 and 45 wt% at 4 and 20 h reaction time, respectively. The monomer conversions of homo polymerizations were found to be quite low, 3 and 12%.

Figure 3 exhibits typical ^{1}H NMR spectrum of PLina-*g*-PSty (PLinaSty-2) graft copolymer sample. ^{1}H NMR spectra of the graft copolymer sample contained characteristic peaks of the related segments: (δ, ppm): 0.9 ppm (–CH_3 of fatty acid macroperoxide); (δ, ppm): 6.5–7.1 ppm (the phenyl protons in polystyrene). ^{1}H NMR was also used to determine the PLina-

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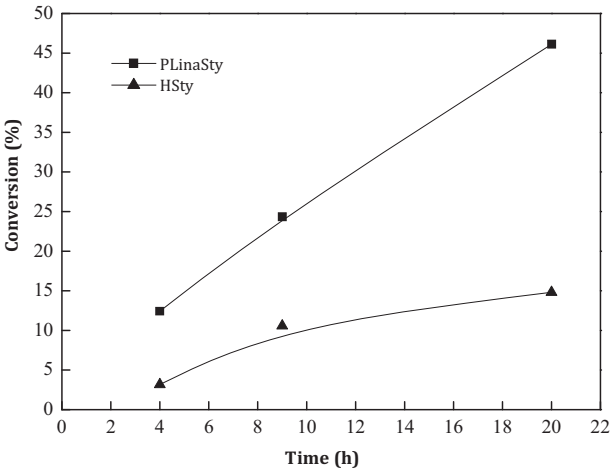

Figure 2. Percentage value of conversion of PLina-g-PSty and homo polystyrene versus polymerization time.

ox and PSty contents in mol% by calculating the peak areas of the methyl protons in PLina-ox (0.9 ppm) and phenyl protons in polystyrene (6.5–7.2 ppm) (given in Table 1).

Polymerization reaction conditions and yields of PLina-*g*-PSty-*g*-PF_5Sty are summarized in Table 2. Figure 4 shows molecular weight and polydispersity versus polymerization time. Molecular weight of graft copolymers measured by GPC technique varied from 1270 to 9140 Da. M_n and M_w values of graft copolymers increase with increasing polymerization time. Polydispersity indices of graft copolymers show a variation in the range of 1.08–1.57. Polymerization reaction is carried out at various times such as 4, 8, 10, 20, 25, and 30 h. Weight percentages of each block of PSty and PF_5Sty in the structure of graft copolymers were also determined from

Table 2. Reaction conditions and characterization of PLina-g-PSty-g-PF_5PSt graft copolymers

Run No.[a]	Time (h)	PF_5Sty (%)[b]	PSty (%)[b]	$M_{n,GPC}$	$M_{w,GPC}$	PDI
PLinaStF_5St-1	4	4.2	2.82	1270	1490	1.18
PLinaStF_5St-2	8	11.1	9.86	4390	4730	1.08
PLinaStF_5St-3	10	19.4	15.49	5960	6620	1.11
PLinaStF_5St-4	20	38.9	36.62	7860	10030	1.28
PLinaStF_5St-5	25	47.2	47.89	8750	11520	1.32
PLinaStF_5St-6	30	49.3	49.27	9140	12400	1.36

[a]All polymerization were carried out in 70% (v/v) anisole with PLina-ox:0.5 g, F_5Sty:1.8 g, Sty: 1.51 g, and [PLina-ox]:[TEMPO]:[Sty]:[F_5PSty][1]:[1]:[50]:[50] at 130°C.
[b]Determined by ^{1}H NMR.

^{1}H NMR. Figure 5 also shows monomer conversion percentages of tri block graft copolymers. Percentage values of PSty and PF_5Sty in the graft copolymer have increased according to increased polymerization time. The percentage of the amount of PSty and PF_5Sty in graft copolymer is found to be changing in the range of 2.82–49.27% and 4.16–49.27%, respectively.

Figure 6 exhibits typical ^{1}H NMR spectrum of PLina-*g*-PF_5Sty-*g*-PSty (PLinaStF_5St-6) graft copolymer sample. ^{1}H NMR spectra of the graft copolymer sample contained characteristic peaks of the related segments: (δ, ppm): 0.9 ppm (–CH_3 of fatty acid macroperoxide); (δ, ppm): 6.5–7.1 ppm (the phenyl protons in polystyrene). Unfortunately, we could not observe the PF_5Sty segment in graft copolymer using ^{1}H NMR as PF_5Sty does not contain any specific protons in its structure. However, we could observe monomer conversion from ^{1}H NMR because vinyl groups of Sty and F_5Sty have separate peaks in ^{1}H NMR.

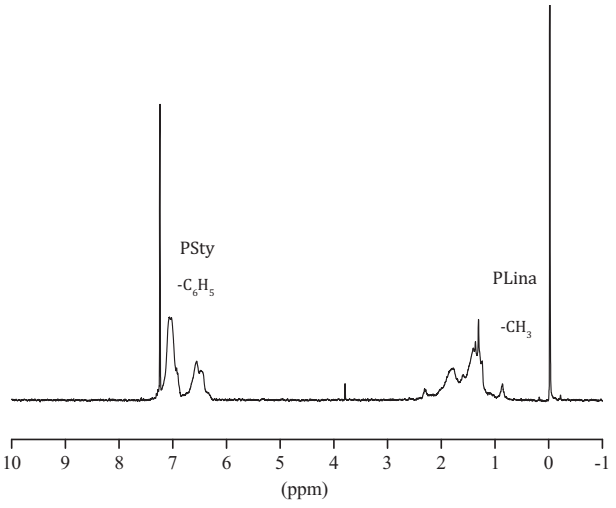

Figure 3. ^{1}H NMR spectrum of PLina-g-PSty graft copolymer (PLinaSty-3).

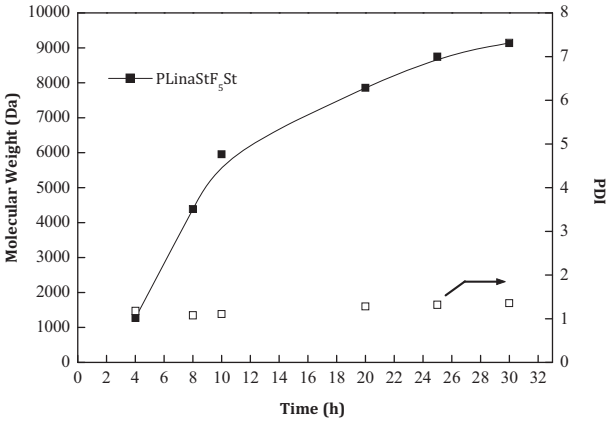

Figure 4. Variation of molecular weight (M_n) and polydispersity versus the polymerization time of PLina-g-PF_5Sty-g-PSty graft copolymer.

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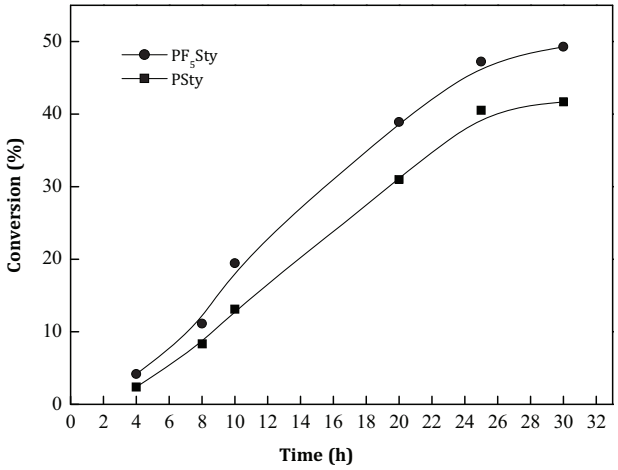

Figure 5. Percentage value of conversion of PLina-g-PF_5Sty-g-PSty versus polymerization time.

Figure 7 shows ^{1}H NMR spectrum of PLina-*g*-PF_5Sty-*g*-PSty (PLinaStF_5St-2) graft copolymer which is taken directly from the Schlenk tube. This polymerization mixture contains polymer, Sty, and F_5Sty monomers. Thus, we could measure the percentages of the monomer conversion. We have also confirmed the successful synthesis of PLina-*g*-PF_5Sty-*g*-PSty graft copolymer as we have measured ^{19}F NMR of PLinaStF_5St-6 sample. Figure 8 shows the ^{19}F NMR spectrum of PLina-*g*-PSty-*g*-PF_5PSt graft copolymer (PLinaStF_5St-6). In this spectrum, we have observed tri peaks of fluoride corresponding for orto-, meta-, and para- positions. ^{19}F NMR spectra of the graft copolymer sample (PLinaStF_5St-6) contained characteristic peaks of the related segments: (δ, ppm): −142 ppm (orto-fluoride), −158 ppm (meta-flouride), and −164 ppm (para-flouride) [32, 34].

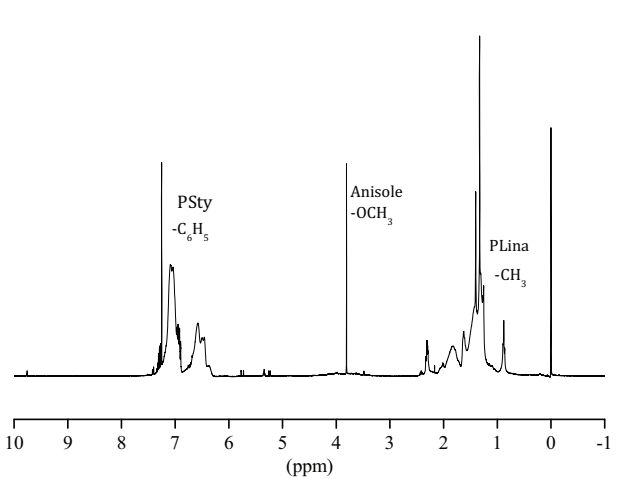

Figure 6. ^{1}H NMR spectrum of PLina-g-PSty-g-F_5Sty graft copolymer (PLinaStF_5St-6).

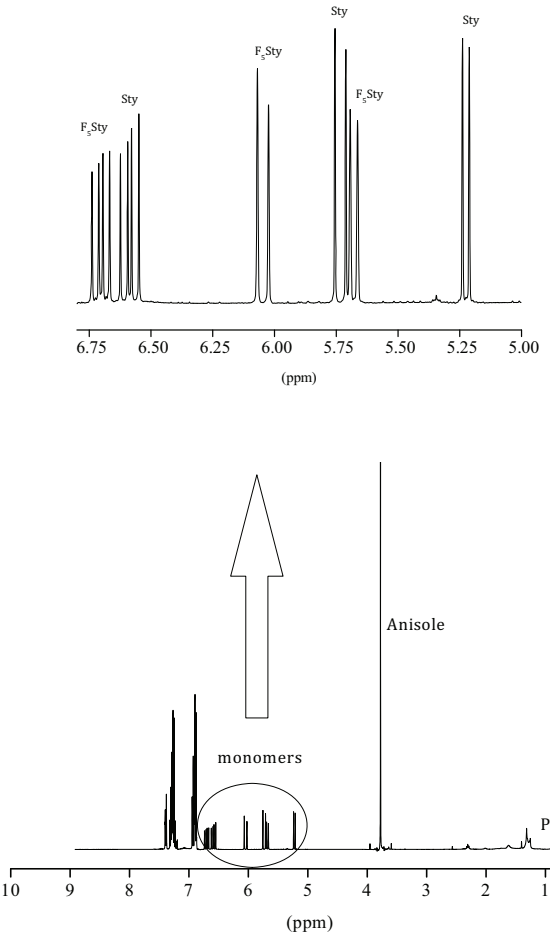

Figure 7. ^{1}H NMR spectrum of PLina-g-PSty-g-F_5Sty graft copolymer (PLinaStF_5St-2) taken from reaction for 8 h.

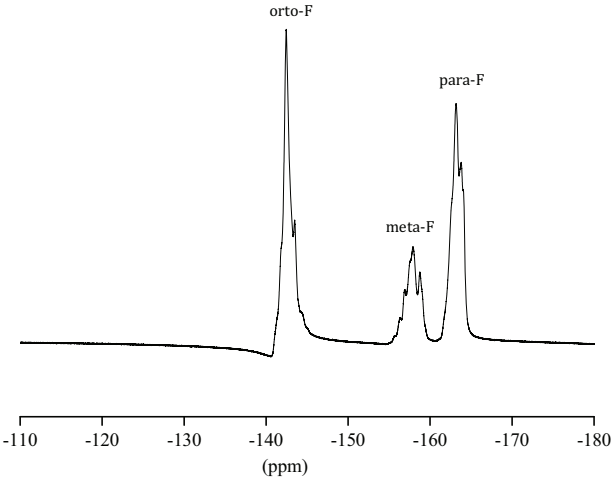

Figure 8. ^{19}F NMR spectrum of PLina-g-PSty-g-F_5Sty graft copolymer (Run no: PLinaStF_5St-6).

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Table 3. Reaction conditions chain extended PLina-g-$(PSty)_n$ graft copolymers

Run No.[a]	Time (h)	$M_{n,GPC}$	$M_{w,GPC}$	PDI
PLina$(PSt)_n$-0	0	7420	9240	1.25
PLina$(PSt)_n$-1	4	7700	10810	1.40
PLina$(PSt)_n$-2	8	12280	17260	1.41
PLina$(PSt)_n$-3	10	13920	21380	1.53
PLina$(PSt)_n$-4	20	15690	25380	1.62
PLina$(PSt)_n$-5	25	16080	25640	1.59

[a]All polymerization were carried out in 50% (v/v) anisole with PLina-g-PSty:0.5 g and Sty:1.73 g at 130°C.

To understand the NMRP system we have further studied chain extension of PLina-*g*-PSty graft copolymer. Chain extension reaction conditions are shown in Table 3. The SEC profile of chain extension of PLina-*g*-PSty graft copolymers with styrene is shown in Fig. 9. Figure 10 shows molecular weight and polydispersity versus polymerization time. Chain extension reaction was carried out at various times such as 4, 8, 10, 20, and 25 h. Molecular weight of graft copolymers measured by GPC technique varied from 7420 to 16080 Da. M_n and M_w values of graft copolymers increase with increasing polymerization time. Polydispersities of graft copolymers show a variation in the range of 1.25–1.62.

Figure 11 exhibits typical ^{1}H NMR spectrum of chain extended PLina-*g*-$(PSty)_n$ (PLina$(PSt)_n$-5) graft copolymer sample. ^{1}H NMR spectra of the graft copolymer sample

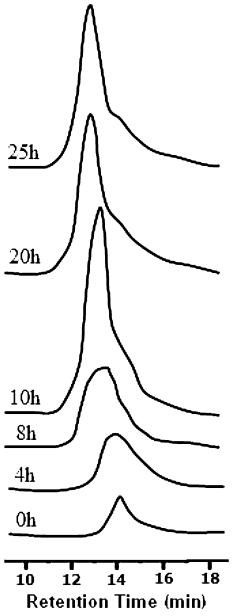

Figure 9. SEC profiles of chain extended PLina-g-$(PSty)_n$ graft copolymer at various times.

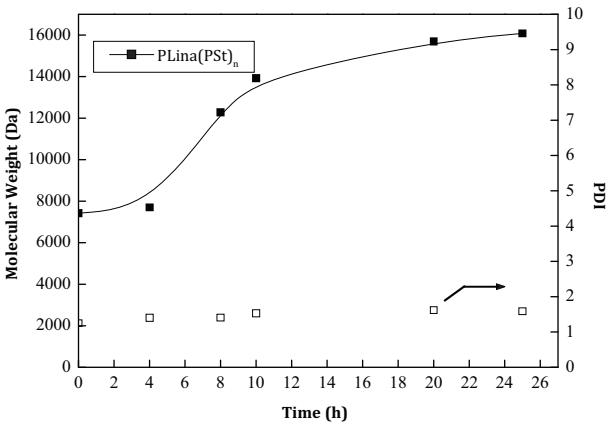

Figure 10. Variation of molecular weight (M_n) and polydispersity versus the polymerization time of chain extended PLina-g-$(PSty)_n$ graft copolymer.

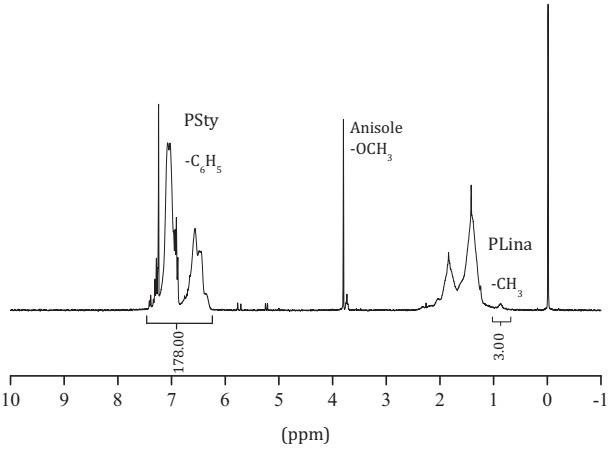

Figure 11. ^{1}H NMR spectrum of chain extended PLina-g-$(PSty)_n$ graft copolymer (Run no: PLina$(PSt)_n$-5).

contained characteristic peaks of the related segments: (δ, ppm): 0.9 ppm (–CH_3 of fatty acid macroperoxide); (δ, ppm): 6.5–7.1 ppm (the phenyl protons in polystyrene). When Fig. 11 and Fig. 3 are compared with each other their integrations are particularly different. It is seen that PSty integration of chain extended polymer has been increased particularly.

4 Conclusions

In conclusion, we have demonstrated for the first time the synthesis of PLina-*g*-PSty and PLina-*g*-PSty-*g*-PF_5Sty graft copolymers in the presence of TEMPO and their chain extension. Pure linoleic acid was auto-oxidized under

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daylight and air oxygen, yielding peroxidized PLina (PLina-ox). PLina-ox has been used for the polymerization of Sty or Sty and F_5Sty in the presence of TEMPO. The NMRP method has been utilized in order to obtain PLina-*g*-PSty and PLina-*g*-PF_5Sty-*g*-PSty graft copolymers with controlled structure and low polydispersity. Chain-extension reactions were also successfully carried out because of the activation of TEMPO-terminated chain ends of graft copolymers. Higher molecular weights of samples were obtained.

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