J Am Oil Chem Soc (2011) 88:255–263
DOI 10.1007/s11746-010-1663-1

ORIGINAL PAPER

Synthesis and Characterization of Poly(*N*-Isopropyl Acryl Amide)-g-Poly(Linoleic Acid)/Poly(Linolenic Acid) Graft Copolymers

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Received: 26 May 2010 / Revised: 16 July 2010 / Accepted: 23 July 2010 / Published online: 27 August 2010
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Abstract To diversify edible oil thermoresponsive polymer composites, polymeric linoleic acid peroxide (PLina) and polymeric linolenic acid peroxide (PLinl) were obtained by the autoxidation of linoleic acid (Lina) and linolenic acid (Linl), respectively. The autoxidation of Lina and Linl under air at room temperature rendered waxy soluble polymeric peroxide, having a soluble fraction in chloroform of more than 91 wt% and containing up to 1.0 wt% of peroxide. The soluble polymeric oil macroperoxide was used to initiate the free radical polymerization of *N*-isopropylacrylamide, NIPAM, resulting in PLina-g-PNIPAM and PLinl-g-PNIPAM graft copolymers, respectively. The PNIPAM content of the graft copolymers was calculated using the elemental nitrogen analysis of graft copolymers. Thermal analysis, FTIR, ^{1}H NMR, and SEM techniques were used in the characterization of the products. The hydrophobic effect of the fatty acid macro peroxides on the thermal response rate of the graft copolymers was investigated by means of swelling-deswelling behaviors in response to temperature change. They have a thermoresponsive character and exhibit a volume phase transition at approximately 27–30 °C, which is 1–4 °C lower than that of pure PNIPAM. A plastizer effect of PLina and PLinl in graft copolymers was observed, indicating a lower glass transition temperature than that of pure PNIPAM.

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Keywords Autoxidation · Linoleic acid · Linolenic acid · *N*-isopropylacrylamide · Graft copolymer

Introduction

Stimuli-responsive polymers play an important role in the development of novel smart polymers for biomedical use [1]. Among them, temperature-responsive polymers have been anticipated as a promising material for temperature-modulating controlled release because of their sensitive phase transition behavior. Most of these polymers are produced in the form of homopolymers or copolymers of NIPAM. PNIPAM gel is a well-known temperature-sensitive gel, exhibiting a volume phase transition at approximately its lower critical solution temperature (LCST) at 32 °C. Below this temperature, the gel swells; it shrinks at the higher temperature. These unique characteristics make PNIPAM-based hydrogels especially useful in biomedical applications, such as in the controlled release of drugs and in tissue engineering [2]. The modification of the LCST of temperature-sensitive gels is of primary interest. Incorporation of hydrophobic residues increases the hydrophobicity of the network chains, leading to a decrease in the LCST. Copolymerization of PNIPAM is a useful way to overcome certain limitations. For example, higher or lower response temperatures of the thermoresponsive polymers are generally preferred in most applications. In addition, conjugation has also proved useful in combining the advantageous properties of the individual components. For example, hybrid block and graft copolymers of PNIPAM containing phosphocholine, poly (D,L-lactide), alginate, propyl acrylic acid, cystamine bis acrylamide, segmented polystyrene, and polymeric soybean oil have been successfully synthesized and well characterized [3].

Vegetable oils, such as soybean oil, palm oil, and rapeseed oil, are extracted primarily from the seeds of oilseed plants and have a wide variety of applications [4]. In recent years, natural oils, fatty acids, and their derivatives have attracted significant attention as raw materials for the preparation of monomers and polymeric materials to move toward more environmentally friendly feedstocks [5]. In this manner, polymers and copolymers based on unsaturated oils can be obtained by using several polymerization techniques [6–9].

The macroperoxy initiators are very useful tools in order to obtain block/graft copolymers via free radical mechanisms [10–13]. One way to obtain oil polymer is the autoxidation of the polyunsaturated oil (PUO), which is carried out under air oxygen and sunlight primarily via hydroperoxidation together with peroxidation, epoxidation, and perepoxidation. Macroperoxy initiators are obtained from polyunsaturated oil/oily acids by this method. Porter et al. found that when polyunsaturated fatty acids are exposed to oxidative stress, the primary products are hydroperoxides [14, 15]. This oxidation process is a free radical chain reaction, which targets the nonconjugated diene moieties of PUO [16]. Oxidation is initiated by abstraction of the bis-allylic hydrogen atom generating a radical, which can undergo trapping at either terminus or at the central (bis-allylic) position. These oil/oily acid macroperoxides can initiate the free radical polymerization of vinyl monomers, leading to graft copolymers [17–19]. To the best of our knowledge, there are no papers describing PNIPAM copolymers containing polyunsaturated fatty acids. Therefore, this idea motivated us to prepare PNIPAM-g-PLina and PNIPAM-g-PLinl graft copolymers by the free radical polymerization of NIPAM initiated by PLina and PLinl, respectively. In this paper, in extension of our continuing research on the autoxidation of the oil/oily acids, we describe the polymerization of NIPAM initiated by the macroperoxides PLina and PLnl in order to obtain PNIPAM-g-PLina and PNIPAM-g-PLinl.

Experimental Section

Materials

Linoleic acid (*cis*-*cis*-9-12-octadecadienoic acid) and linolenic acid (*cis*,*cis*,*cis*-9,12,15-octadecatrienoic acid) were supplied from Fluka (Steinheim, Germany), and both were used as received. *N*-Isopropylacrylamide (NIPAM) was supplied from Aldrich. They were purified by means of recrystallization from *n*-hexane and then dried under vacuum at room temperature. All other chemicals were of analytical grade and used as received.

Autoxidation of Linoleic Acid and Linolenic Acid

For the autoxidation of linoleic acid and linolenic acid, the same procedure reported in the literature [18] was used. Briefly, 5.0 g of linoleic acid (or linolenic acid) spread out in a Petri dish ($\varnothing = 5$ cm) was exposed to sunlight in the air at room temperature. A pale-yellow, viscous liquid polymeric linoleic peroxide and a dark, pale-yellow viscous liquid linolenic peroxide were obtained after 2 months autoxidation, respectively. Samples were mostly viscous liquid having cross-linked parts <9 wt%, which were isolated with the chloroform extraction by means of sol-gel analysis.

The Peroxygen Analysis

Peroxide analysis of PLina and PLinl fractions was carried out by refluxing a mixture of 2-propanol (50 ml)/acetic acid (10 ml)/saturated aqueous solution of KI (1 ml) and 0.1 g of the polymeric sample for 10 min and titrating the released iodine against thiosulfate solution, according to the procedure cited in the literature [19]. The peroxygen content of the PLina and PLinl samples was found to be 1.0 and 1.2 wt%, respectively.

Synthesis of the Graft Copolymers

As a typical polymerization, 0.5 g of PLina and 0.5 g of NIPAM were charged separately into a Pyrex tube with a magnetic stirring bar. Argon was introduced through a needle into the tube for about 3 min to expel the air. The tightly capped tube was put in an oil bath at 80 °C for 5 h. Then, the tube content was poured into a large amount of diethyl ether to precipitate crude polymer. In order to remove unreacted monomer from the crude polymer, it was soaked in distilled water for 1 week by changing the solution with pure water at room temperature on a daily basis. The purified copolymer was dried under vacuum at 40 °C.

Instrumentation

The ^{1}H NMR and ^{13}C NMR spectra of the polymers were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) using $CDCl_3$ as solvent. FTIR and FTIR-ATR (attenuated total reflectance spectroscopy) spectra were recorded using a Nicolet 520 model FTIR Fourier Transform Infrared Spectrometer and Perkin Elmer FTIR Spectrometer 100. The FTIR spectra of the graft copolymers were taken as KBr samples.

SEC measurements in tetrahydrofuran (THF), a Polymer Laboratories GPC Setup (gel permeation chromatography),

was used as an integrated instrument, a UV (254 nm) and RI detector. Calibration was carried out using poly(styrene) standards provided by Polymer Laboratories. Molecular weights (MWs) of the seven standards used were 1,260 (PDI 1.06), 4,920 (PDI 1.03), 9,920 (PDI 1.02), 30,300 (PDI 1.02), 60,450 (PDI 1.02), 170,800 (PDI 1.02), and 299,400 (PDI 1.02) g/mol. The eluent (THF) was used at 40 °C at a flow rate of 1 ml/min.

Thermal analysis of the product was carried out by using a Setaram differential scanning calorimetry (DSC) DSC-141 series thermal analysis system under nitrogen. In a typical experiment, the polymer sample was dried for 24 h in a vacuum oven at 40 °C. Then 10 mg of the sample was sealed in an aluminum DSC pan and heated from −50 to 150 °C at a rate of 10 °C/min under N_2 atmosphere. The midpoint of the sharp curve was marked as Tg [3].

The thermal decomposition of the samples was investigated using a DuPont 951 thermo-gravimetric analyzer; 10 mg of the sample was sealed in an aluminum DSC pan and heated from 20 to 600 °C at a rate of 10 °C/min under N_2 atmosphere. The CHNS-932 Model LECO Elemental Analyzer was used for the elemental analysis of C, H, and N in the products. Molar fractions (mol%) of comonomer units in PLina-g-PNIPAM and PLinl-g-PNIPAM copolymers were calculated using elemental analysis data (content of N). Surface topography of the products was carried out by using a JEOL FEG-SEM JSM 6335F Scanning Electron Microscope (SEM). The specimens were frozen under liquid nitrogen, then fractured, mounted, and coated with gold (300 Å) on an Edwards S 150 B sputter coater. The SEM was operated at 10 kV, and the electron images were recorded directly from the cathode ray tube on a Polaroid film. The magnification employed was varied up to 10,000×; however, both 1,000× and 10,000× magnifications proved useful.

Measurement of Swelling Ratio

The degree of swelling ratio of copolymers was measured gravimetrically in distilled water at temperatures ranging from 4 to 40 °C [20]. Before measuring the swelling ratio, the copolymer was incubated in distilled water for at least 24 h at every particular temperature and weighed after blotting the excess surface water. The swelling degree was defined as follows [21]:

$$\text{Swelling ratio } (\%) = 100 \times (W_s - W_d)/W_d \quad (1)$$

where W_s is the weight of the swollen polymer at a particular temperature, and W_d is the dry weight of the polymer after drying overnight under vacuum.

Measurement of Deswelling Kinetics

The deswelling kinetics of the polymer samples were followed by applying a temperature change in the opposite direction of the swelling behavior investigation. The polymer samples were equilibrated in distilled water at 4 °C and were subsequently transferred into 50 °C distilled water. At each of the selected time intervals, the samples were removed from the hot water and weighed after wiping off the excess water on the surface with a filter paper. Copolymer shrinkage was established by determining the decrease in water content of the polymer samples. The weight of the gels was recorded at predetermined times. The deswelling ratio is defined as:

$$DS = (W_t - W_d)/(W_{o(4\,^\circ C)} - W_d) \quad (2)$$

where DS is the deswelling ratio, $W_{o(4\,^\circ C)}$ is the weight of the polymer at equilibrium at 4 °C, W_t, is the weight of the polymer at a particular time, and W_d is the dry weight of the polymer sample.

Hydrolysis of Graft Copolymer

A piece of graft copolymer (0.5 g) was dissolved in 30 ml of 0.1 M NaOH in ethanol. The reaction mixture was stirred at room temperature for 1 day. The product was filtered, evaporated, and dried under vacuum at 40 °C.

Solubility Test of the Graft Copolymer

For the solubility measurement, the residue of the graft copolymer hydrolyzed in buffer solutions at different pHs was soaked in water, methanol, ethanol, isopropyl alcohol, chloroform, tetrahydrofuran (THF), and toluene for a day. The solubility of the residue was determined visually.

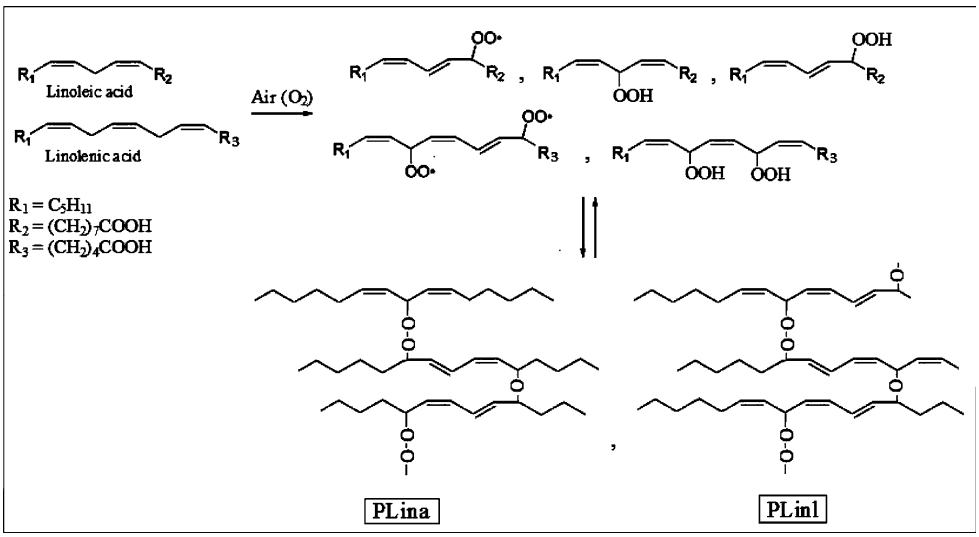
Results and Discussion

The Macroperoxy Initiators from Polyunsaturated Fatty Acids (PLina and PLinl)

Linoleic acid and linolenic acid were exposed to air under sunlight for 2 months to obtain fatty acid macro peroxides. Oxidation was initiated by abstraction of the allylic hydrogen atom, generating a radical that can react with O_2. Scheme 1 shows the theoretical structural model depicting the polymerization and peroxidation of the polyunsaturated fatty acids.

PLina and PLinl were mostly viscous liquids having cross-linked parts <9 wt%, which were isolated with the chloroform extraction. The peroxygen contents of the

Scheme 1 Theoretical structural model depicting the polymerization and peroxidation of the polyunsaturated fatty acids

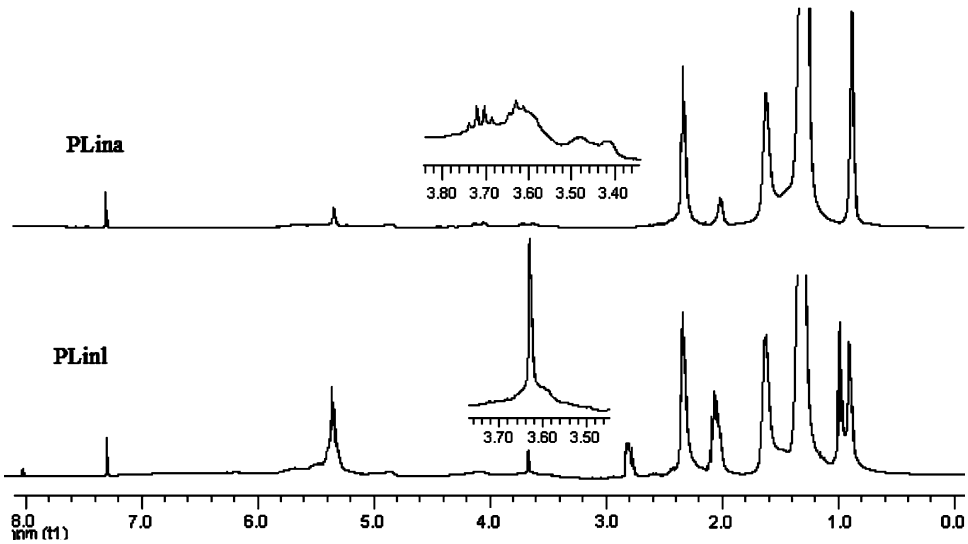


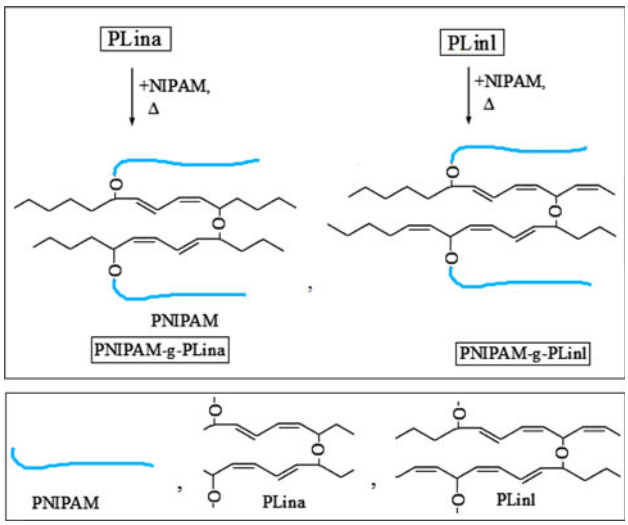
PLina and PLinl were found to be 1.0 and 1.2 wt%, respectively. Molecular weights (MW) of the fatty acid macroperoxides were measured as Mn, Mw, and poly dispersity (PDI) by using gel permeation chromatography: for PLina, 4,977 (Mn), 20,603 (Mw), 4.14 (PDI); for PLinl: 6,549 (Mn), 26,543 (Mw), 4.05 (PDI). GPC curves of the fatty acid macroperoxides were bimodal. During autoxidation, the thickness of the liquid polyunsaturated fatty acid in a Petri dish acts effectively on the MW of the macroperoxide formed. We will report this in a later manuscript. ^{1}H NMR spectra of the polyunsaturated fatty acids had the signals of –CH–O– oxide groups formed by autoxidation at the chemical shifts between 3.4 and 3.8 ppm. Figure 1 shows the ^{1}H NMR spectra of PLina and PLinl.

Graft Copolymerization

Because of their peroxide groups, PLina and PLinl samples initiated the copolymerization of NIPAM at 80 °C, leading to PLina-g-PNIPAM and PLinl-g-PNIPAM graft copolymers in high yield. Scheme 2 shows the reaction design of NIPAM polymerization initiated by the macroperoxides, PLina and PLinl. The copolymerization conditions and copolymer analysis are listed in Table 1. All copolymers obtained were soluble in chloroform and toluene, but not in water. Polymer yields increased by the increase in NIPAM feeding. The average molecular weight (MW) of the copolymers was between 22,500 and 131,000 g/mol. PLinl-g-PNIPAM graft copolymers indicated higher molecular weights than those of PLina-g-PNIPAM. Because linolenic

Fig. 1 ^{1}H NMR spectra of PLina and PLinl





Scheme 2 Reaction design of the polymerization of NIPAM initiated by the fatty acid macroperoxides

acid has a higher unsaturation, autoxidation of the linolenic acid causes higher peroxidation than for linoleic acid. As we know from conventional free radical polymerization, higher peroxide content causes a polymer with lower molecular weight [10, 13]; the MW of the copolymer obtained from PLinl was lower than that of the copolymer obtained from PLina. Elemental nitrogen analysis of PNIPAM segments in the graft copolymers was useful in determining the PNIPAM content of the graft copolymer. Elemental nitrogen analysis of PNIPAM blocks gave the NIPAM amount in the graft copolymer using the following equation:

$$\text{NIPAM, mol\%} = (\text{N}/\text{No}) \times 100 \quad (3)$$

where N is the wt% of nitrogen content in the graft copolymer determined by the elemental analysis, and No is the wt% of nitrogen content of the pure PNIPAM (12.4 wt%). The PLina and PLinl content of the PLina-g-PNIPAM and PLinl-g-PNIPAM graft copolymer can also simply be determined by the equation given below:

$$\text{PLina (or Plinl), mol\%} = 100 - \text{NIPAM, mol\%} \quad (4)$$

The varying polymer yield and its PLina and PLinl content as related to the initial feed ratio of NIPAM are also presented in Table 1. Based on elemental analysis, these graft copolymers contained 37–76 wt%, depending on the initial feed ratio. The N-content of the copolymer rises with the increase in the initial feed ratio of NIPAM.

The FTIR spectra of the graft copolymers were taken as KBr samples. Figure 2 shows the FTIR spectra of a typical graft copolymer (Leic-2 in Table 1) together with the related homopolymers.

The PNIPAM-g-fatty acid graft copolymers had characteristic signals at 1,660 cm^{-1} and 3,320 cm^{-1} (–CO–NH–), which confirmed the presence of PNIPAM. The graft copolymers also had characteristic signals at 1,740 cm^{-1} (–C=O, ester groups of PLina and PLinl).

PLina-g-PNIPAM and PLinl-g-PNIPAM graft copolymer samples were also characterized by using ^{1}H NMR spectroscopy. Figure 3 shows a typical ^{1}H NMR spectrum of a PLina-g-PNIPAM graft copolymer sample (Leic-3 in Table 1). ^{1}H NMR spectra of the graft copolymer samples contained characteristic peaks of the related segments: (δ, ppm): 5.6–6.3 ppm (the vinyl protons of the fatty acid macroperoxides), 2.3 ppm (–C**H**$_2$–COOH of fatty acid macroperoxide) and 3.8–4.1 ppm –CH–NH–. PNIPAM content in the graft copolymer sample was also calculated by comparing integral ratios of the signal at 4.1 ppm with that of the signal at 2.3 ppm. The results of PNIPAM content calculated by ^{1}H NMR were in good agreement with the results calculated by elemental nitrogen analysis (Table 1).

Thermal Analysis of the Graft Copolymers

Thermal analysis of graft copolymers was performed by DSC and TGA to determine the glass transition temperature (T_g) and decomposition temperatures (T_d), respectively. Figure 4 shows the DSC traces of the PNIPAM graft copolymers. A dramatic plasticizer effect of fatty acid macro peroxides was clearly observed. T_gs of the

Table 1 Reaction conditions and polymerization results of the synthesis of PNIPAM graft copolymers

Run no.	PLina (g)	PLinl (g)	NIPAM (g)	Polym Yield (g)	NIPAM (%)[a]	NIPAM (%)[b]	Mn $\times 10^3$	MW $\times 10^3$	P.D.I.
Leic-1	0.50	–	0.50	0.50 ± 0.11(3)	56	50	9.63	31.3	3.25
Leic-2	0.51	–	1.00	0.89 ± 0.08(3)	66	59	36.4	64.9	1.78
Leic-3	0.50	–	2.00	1.76 ± 0.14(3)	76	70	83.2	131	1.57
Lenic-1	–	0.50	0.50	0.35 ± 0.05(3)	37	35	8.12	22.5	2.77
Lenic-2	–	0.50	1.00	0.97 ± 0.12(3)	58	65	20.8	43.3	2.08
Lenic-3	–	0.50	2.00	1.32 ± 0.16(3)	67	53	41.5	73.9	1.78

[a] Calculated from elemental analysis

[b] Calculated from ^{1}H NMR

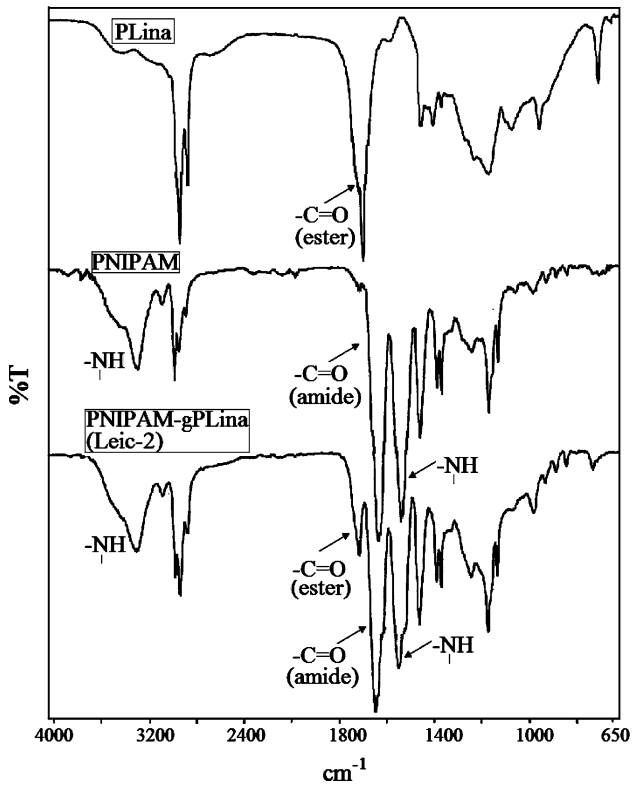


Fig. 2 FTIR spectra of PLina, PNIPAM and PLina-g-PNIPAM graft copolymer sample (Leic-2)

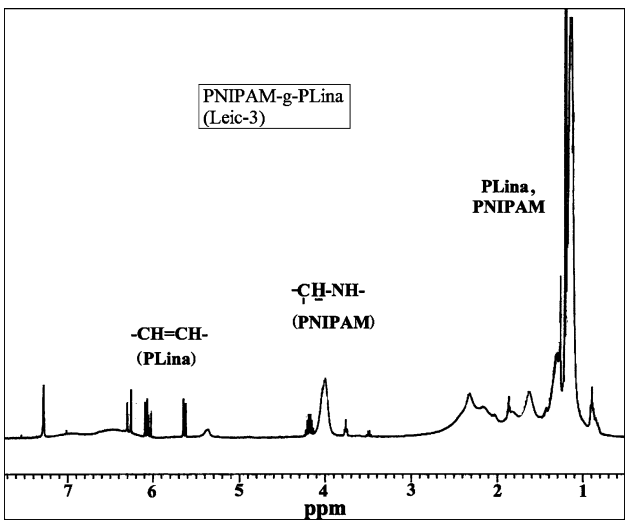


Fig. 3 ^{1}H NMR spectrum of PLina-g-PNIPAM graft copolymer (Leic-3 in Table 1)

copolymers were observed between 50 and 56 °C, which was lower than for the PNIPAM homopolymer (T_g = 135 °C).

Thermal characterization of copolymers was further achieved by recording their weight loss curves with temperature. Table 2 shows the DSC and TGA thermal

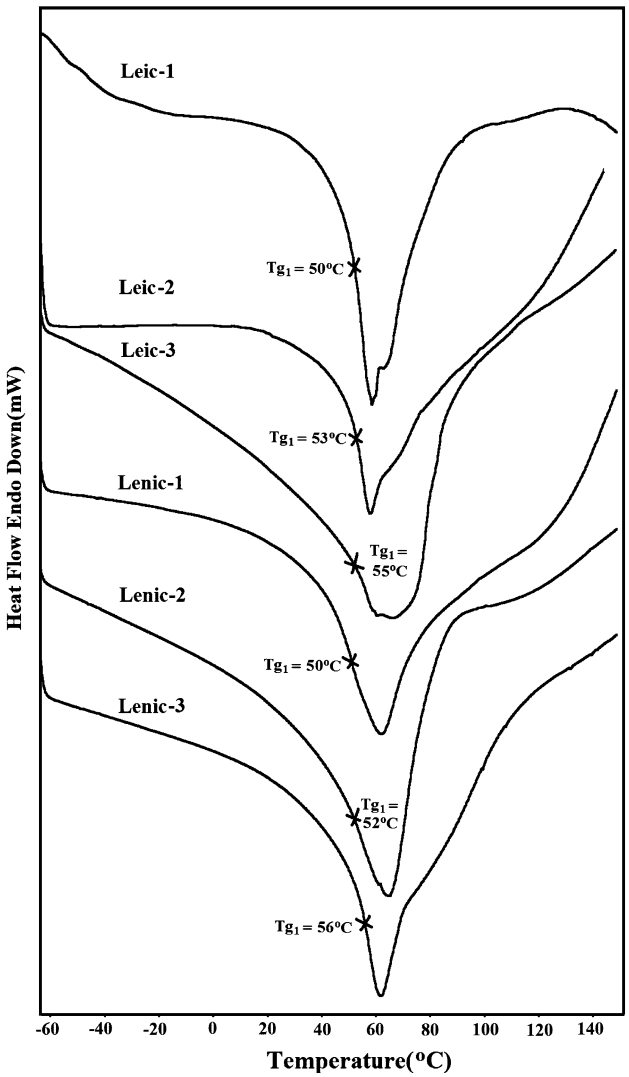


Fig. 4 DSC traces of the graft copolymers. (For sample abbreviations, see Table 1)

Table 2 DSC and TGA thermal analysis results of the graft copolymers

Sample	DSC (°C)		TGA (°C)		
	T_m	T_{g1}	T_{d1}	T_{d2}	T_{d3}
Leic-1	–	50	–	340	395
Leic -2	–	53	–	340	410
Leic-3	–	55	–	340	425
Lenic-1	–	50	–	335	405
Lenic-2	–	52	–	340	410
Lenic-3	–	56	–	340	415
PNIPAM [23]	–	135	–	–	431
Fatty acid macro peroxides	29	–	170	353	463

analysis results of the graft copolymers. Decomposition temperatures of the two segments in the graft copolymers were observed at around the same temperature ranges.

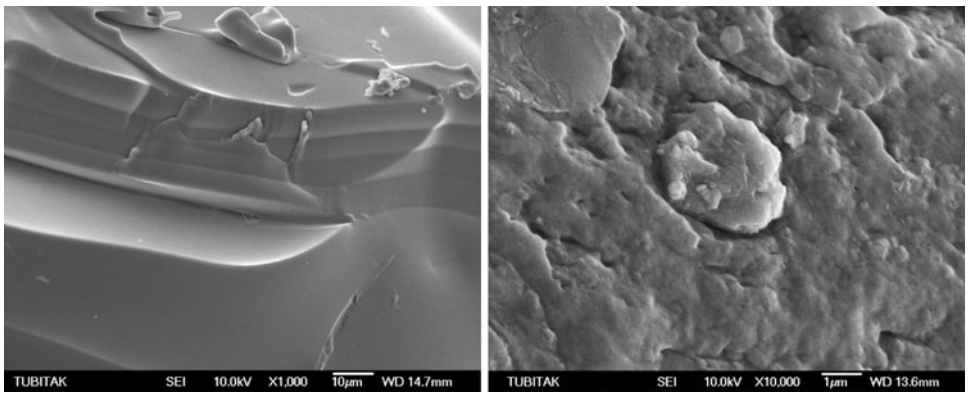


Fig. 5 SEM micrographs of a typical copolymer sample (PLina-g-PNIPAM Leic-1 in Table 1) at different magnifications: bars show 10 μm (**a**) and 1 μm (**b**)

Because of the plasticisizing effect of the fatty acid macro peroxides, PLina and PLinl blocks reduced the decomposition temperatures of the PNIPAM segments, 10–20 °C.

SEM Analysis

The series of graft copolymer were also analyzed by taking SEM micrographs. Figure 5 shows a SEM micrograph of a PLina-g-PNIPAM copolymer sample (Leic-1 in Table 1) in different magnifications. SEM micrographs of the copolymer samples indicated the continuous polymer matrix, which could be attributed to both segments being well mixed in the copolymer structure.

Hydrolysis of the Graft Copolymers

The graft copolymers were soluble in methanol, ethanol, isopropyl alcohol, and THF; insoluble in water and toluene; and partially soluble in chloroform. For the hydrolysis experiment, a graft copolymer sample (Leic-2 in Table 1) was soaked in different ethanol buffer solutions at pH 7, 11, 12, and 13 for a day. Copolymer residue hydrolyzed at pH 13 was soluble in water, whereas the residues hydrolyzed at pH 11 and 12 were not soluble in water. This indicated that the copolymer residue hydrolyzed at pH 13 is pure PNIPAM peeling off the fatty acid segments. This was also confirmed by taking ^{1}H NMR spectra of the copolymer residues hydrolyzed at pH 12 and 13 (Fig. 6). The signals of the vinyl protons at 5.7–6.3 ppm almost disappeared in Fig. 6a.

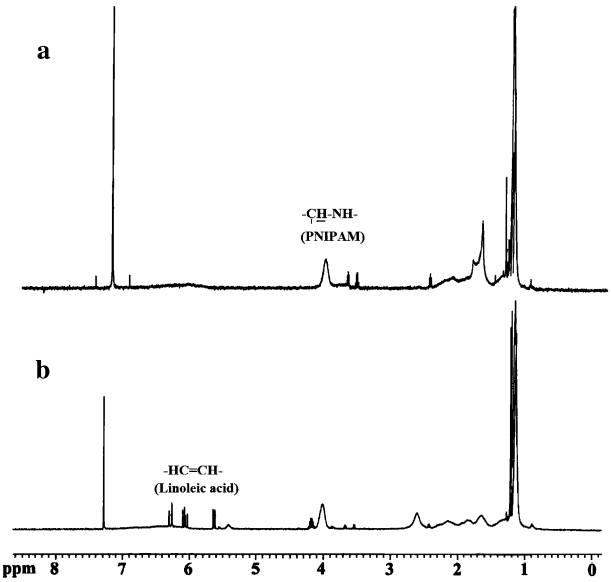


Fig. 6 ^{1}H NMR spectra of the copolymer (Leic 2 in Table 1) residue hydrolyzed at pH 13 (**a**) and at pH 12 (**b**) in ethanol buffer solutions

Swelling Behaviors

PLina-g-PNIPAM and PLinl-g-PNIPAM

Incorporating more hydrophilic or hydrophobic monomers into the gel compositions can control phase transition behavior. It is known that hydrophilic groups (–CONH–) and hydrophobic groups (–$CH(CH_3)_2$) are found in NIPAM, corresponding to the hydrophilic and hydrophobic regions, respectively, in the PNIPAM hydrogel [22]. Increasing the number of hydrophobic units will decrease the hydrophilicity of the whole gel network, leading to a decreased swelling ratio of the hydrogel at temperatures below the LCST and shifting the transition temperature to the lower LCST values.

The degree of swelling of the copolymers was determined between 4 °C and 40 °C. The temperature dependence of the equilibrium swelling ratio of PNIPAM graft copolymers are given in Fig. 7.

Increasing the hydrophobic segment content in the gel copolymer causes a dramatic decrease in the swelling degree down to 1,000 from 2,400%. From the plots of swelling degree versus temperature, we found the LCSTs of the copolymers to be 30 and 29 °C for Leic-3, Leic-2, and 28 and 27 °C for Lenic-3 and Lenic-2, respectively, corresponding to the increasing content of hydrophobic units (PLina and Plinl in Table 1). The samples containing

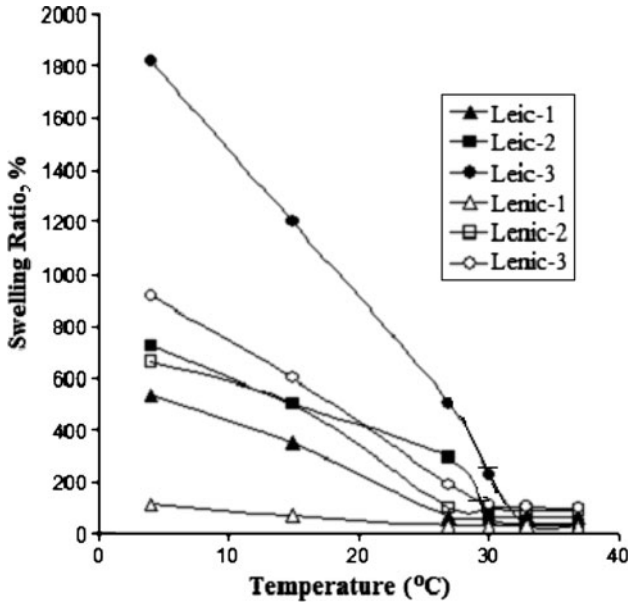


Fig. 7 Equilibrium swelling ratio of the copolymers in water as a function of temperature. LCSTs of the copolymers were found to be 1–4 °C lower than that of PNIPAM. The samples containing higher amounts of PLina and PLinl (Leic-1 and Lenic-1) do not have thermoresponsive properties

higher amounts of PLina and PLinl (Leic-1 and Lenic-1) did not have thermoresponsive properties.

Deswelling Behaviors

In order to follow the shrinkage kinetics of the copolymers, the step input at medium temperature was applied in the reverse direction [22]. Polymer samples were swollen at 4 °C, and shrinking experiments were carried out at 50 °C, according to the procedure cited in reference [3]. Figure 8 shows the time dependence curves of the deswelling ratios of PNIPAM graft copolymers. Deswelling behaviors of the copolymers after a temperature jump from the equilibrated swollen state at 4 °C to hot water at 50 °C are displayed in Fig. 8. As can be seen in this figure, the quickest shrinkage was observed in the NIPAM-rich copolymer samples, which reach the equilibrium state first. Leic-3 and Lenic-3 exhibit a dramatically faster response rate to temperature changes. Leic-3 loses 95% in 1 min and over 98% in 5 min. Lenic-3 loses 90% in 1 min and over 95% in 5 min. Lenic-2 loses 82% in 1 min and over 85% in 5 min. Leic-2 loses 88% in 1 min and over 90% in 5 min.

Conclusions

The combination of different polymeric blocks in the responsive thin film results in a broadening of the switching range of properties, so that the surface property of the

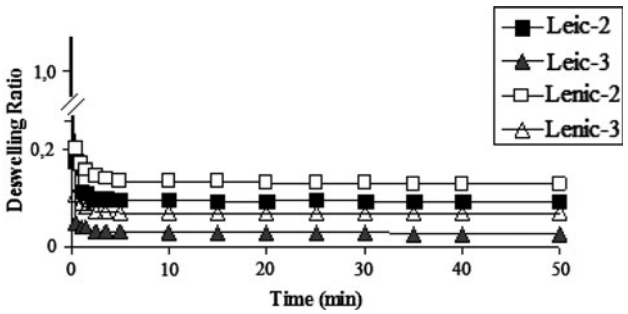


Fig. 8 Shrinking kinetics for the graft copolymers. Time dependence of the deswelling ratios of PNIPAM graft copolymers in distilled water at 50 °C. The polymer samples were first equilibrated in water at 4 °C. The samples were then moved into water at 50 °C. At specific times, these samples were removed from the water and weighed after being wiped with filter paper to remove excess water on the surface. The shrinking kinetics are defined as the changes with time in the swelling ratios for the polymer samples

film changes from the property of one polymer to that of the second polymer, or is locked in some intermediate state. Pure linoleic and linolenic acid can be polymerized under sunlight and air oxygen, yielding peroxidized PLina and PLinl, respectively. This polymerization system does not need any metal catalyst or solvent, making this procedure important for medical applications of the graft copolymers. The novel thermoresponsive graft copolymers are obtained by the polymerization of NIPAM initiated by PLina and PLinl, leading to PLina-g-PNIPAM and PLinl-g-PNIPAM graft copolymers. These responsive polymers, with fast degradation of the fatty acid segments and the sensitivity of their swelling/deswelling behavior, have potential applications in industry, bioengineering and medicine.

Acknowledgments This work was financially supported by TUBITAK (grant nos. 109T029 and 108T423), Zonguldak Karaelmas University Research Fund (grant no. 2008-70-01-01), and Düzce University Research Fund.

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