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Redox polymerization of N-isopropylacrylamide by using hydroxylated soya oil polymer

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Abstract: Water soluble hydroxylated soya oil polymer was used in the redox polymerization of N-isopropylacrylamide (NIPAM) in order to obtain water-based hydroxylated-soya oil polymer-g-PNIPAM graft copolymer. For this purpose, soya oil was exposed to air under sunlight to obtain autoxidized soya oil polymer (PSy-ox). PSy-ox was allowed to react with diethanol amine to obtain hydroxylated soya oil polymer (hydroxylated-PSy). An ammonium persulfate with hydroxylated-PSy redox initiating system was used in the polymerization of NIPAM in order to obtain thermo-responsive hydroxylated-PSy-g-PNIPAM water-based graft copolymers. The graft copolymers were characterized using proton nuclear magnetic resonance, Fourier transform infrared spectroscopy, gel permeation chromatography, thermal gravimetric analysis, and differential scanning calorimetry techniques. The effects of hydroxylated-PSy on the thermal response rate of PNIPAM and the percentage of transmittance in the water of graft copolymers were studied by means of observing UV transmittance behaviors in response to changing temperature. This showed the temperature-responsive property, and exhibited a volume phase transition from 22 °C to 29 °C, while that of PNIPAM was 32 °C.

Key words: Hydroxylated soya oil polymer, thermo-responsive polymer, N-isopropylacrylamide, redox polymerization

1. Introduction

Soya oil is one of the most abundant and inexpensive renewable sources for the preparation of high molecular weight polymers. It is composed of polyunsaturated fatty acids with the main component being linoleic acid (ca. 50 wt%).[1,2] Air oxygen and sunlight can polymerize soya oil via peroxidation, epoxidation, and perepoxidation to perform polymeric soya oil peroxide (PSy-ox). Autoxidation of polyunsaturated oils can be achieved via hydrogen abstraction from a methylene group between two double bonds.[3−5] These polymeric oil peroxides were used to initiate the free radical polymerization of methyl methacrylate, styrene, and butyl methacrylate to obtain block/graft copolymers containing polymeric oil segments.[6−10]

Hydroxylated soya oils for the preparation of polyurethane materials can be obtained in several ways.[11−18] The PSy-ox can be converted to a polyol by using an Fe(III) catalyst. In that case, the hydroxylated soya oil polymer can swell in water and contains some iron catalyst residue.[19] A novel, completely water-soluble soya oil polymer from the autoxidized soya oil polymeric peroxide and diethanol amine was recently reported by our research group.[20]

Temperature-responsive, aqueous polymer systems are known to show large, reversible, conformational

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changes in response to a small temperature stimuli.[21−27] Poly (N-isopropylacrylamide) (PNIPAM) is the most prominent temperature-responsive (thermo-responsive) polymer, exhibiting a lower critical solution temperature (LCST) at 32 °C.[28−41] At lower temperatures, it is soluble in water, but precipitates at higher temperatures above 32 °C. The modification of temperature-responsive polymer for changing LCST is very interesting.[42−44] Incorporation of the hydrophobic segment in the network chain can accomplish both a decrease in the LCST and an increase in the hydrophobicity of polymer chains.[6,7]

Derivation of PNIPAM is also a helpful path to cope with some restrictions. For example, higher or lower response temperatures of the thermo-responsive polymers are chosen in most applications such as membranes including controlled drug delivery, separation, water treatment, and chemical sensors.[38] Additionally, derivation is also useful to incorporate the favorable properties of the individual segments. For instance, block/graft copolymers of PNIPAM including lionoleic/linolenic acid,[6] soybean oil,[7] phosphocholine,[45,46] poly (D,L-lactide),[47] alginate,[48] propyl(acrylic acid),[49] cystaminebisacrylamide,[50] and component polystyrene have been successfully obtained and well characterized. Either polystyrene or poly (tert-butyl methacrylate) and PNIPAM block branched copolymer's solution properties have been studied in water with significant emphasis on the temperature response of these copolymers.[51]

To the best of our knowledge, hydroxylated soya oil has not been used in any polymerization reaction as a hydrophilic PSy segment in copolymerization in the literature to date. Therefore, this idea motivated us to prepare hydroxylated-PSy-g-PNIPAM graft copolymers by aqueous redox polymerization of NIPAM initiated by hydroxylated-PSy. Because of their hydroxyl groups, hydroxylated-PSy samples initiated the copolymerization of NIPAM at 60 °C in acetone/water solution by using ammonium persulfate (APS), leading to a high yield of hydroxylated-PSy-g-PNIPAM graft copolymers. With this work, two hydrophilic segments (hydroxylated soya oil and NIPAM) were used for the first time to synthesize hydrophilic thermo-responsive soya oil graft copolymers. In addition, redox aqueous polymerization was used for the first time to synthesize hydroxylated-PSy-g-PNIPAM graft copolymers using hydroxylated soya oil.

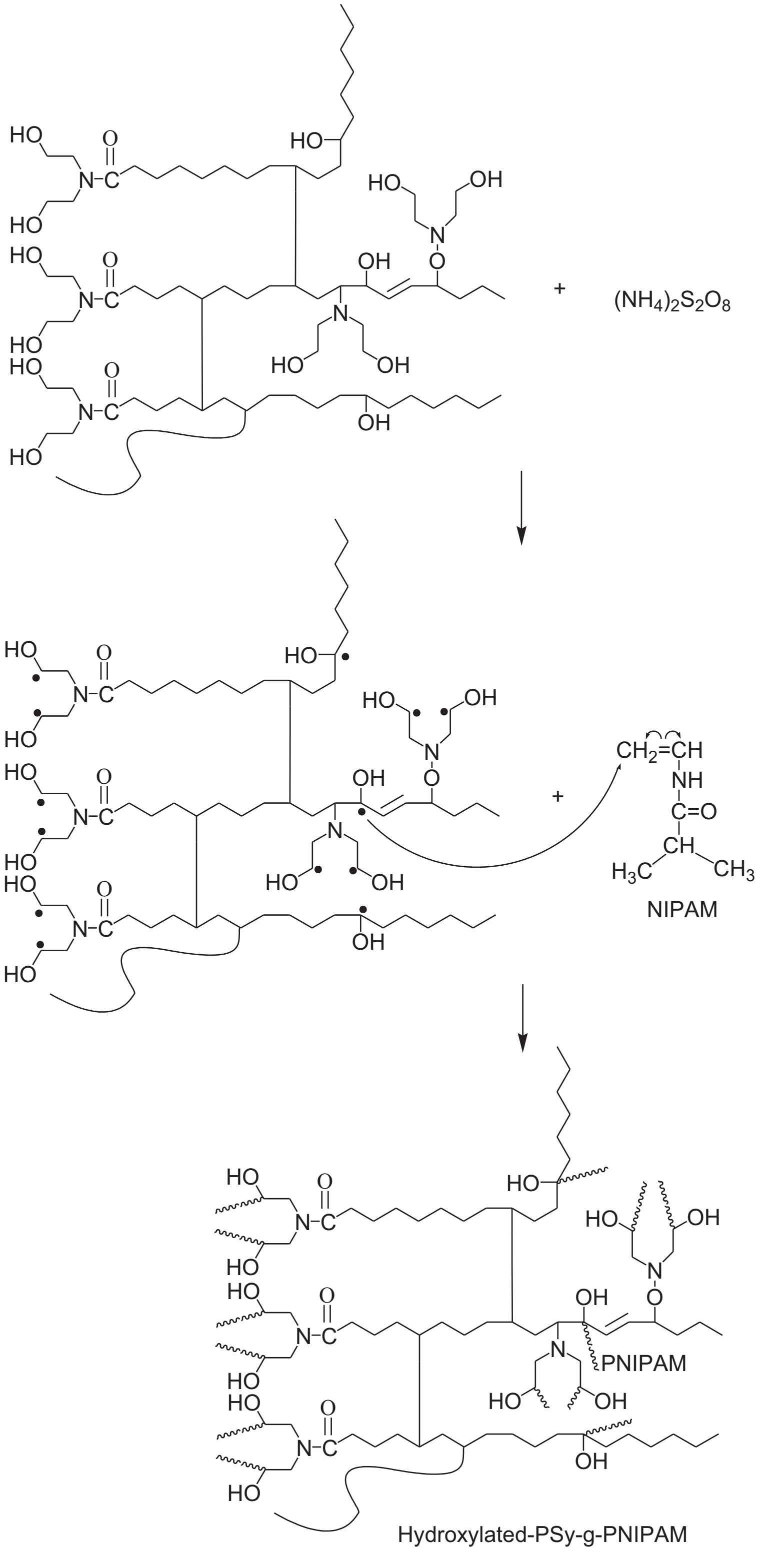
2. Results and discussion

2.1. Hydroxylated soya oil polymers

Soya oil was exposed to air under sunlight to obtain autoxidized soya oil polymer. After the autoxidation process, soya oil polymer (PSy) was used to stimulate a hydroxylation reaction. It was reacted with diethanol amine to obtain hydroxylated-PSy according to the methods described in our previous paper.[20] Molecular weight (MW) of the hydroxylated soya oil was measured as Mn, Mw, and poly dispersity (PDI) using GPC: 5.900 (Mn), 8.800 (Mw), and 1.48 (PDI). The FT-IR spectrum of hydroxylated-PSy using diethanol amine contains alcohol groups at 3300 cm^{-1}, an amide carbonyl group at 1615 cm^{-1}, and C–O bands at 1046 cm^{-1}. In the ^{1}H NMR spectra the hydrolyzed soya oil polymer obtained by using diethanol amine contains (–N CH_2 $\mathbf{CH_2}$ OH) protons, which appeared at 4.1; (C O, C **OH** induced) protons, which appeared at 3.5–3.8; and (N $\mathbf{CH_2}$ CH_2 OH) protons, which appeared at 2.7.

2.2. Graft copolymerization

Hydroxylated soya oil with hydroxyl functional groups was prepared with the aim of further graft copolymerization with NIPAM monomer. Thermo-responsive hydroxylated-PSy-g-PNIPAM graft copolymers were then successfully obtained by using APS as an initiating system. Because of their hydroxyl groups, hydroxylated-



Scheme. Reaction design of the redox polymerization of N-isopropylacrylamide initiated by hydroxylated polymeric soya oil.

PSy samples initiated the copolymerization of NIPAM at 60 °C in an acetone/water solution, leading to a high yield of hydroxylated-PSy-g-PNIPAM graft copolymers. The Scheme shows the reaction design of the redox polymerization. The copolymerization conditions and copolymer analysis are listed in Table 1. The diversifying polymer yield and its hydroxylated-PSy content as related to the initial feed ratio of NIPAM are also given in Table 1. Generally, this polymerization system gives moderate polymer yields (61–98%w/w). The yields of the copolymer increase with the increase in the initial feed ratio of NIPAM. For example, when the copolymers with the same polymerization time and medium conditions but with different PNIPAM initial feed ratios (Tpys-N11-Tpys-N15 series) are considered, it is seen that the polymer yield for higher feed ratio is higher than that of the lower one. This situation is similar to that in our previous study.[7] It can be concluded that a higher monomer concentration leads to good polymerization and gives higher polymer yield. Otherwise, a higher hydroxylated-PSy initial feed ratio gives lower polymer yield because of the formation of more radicals in polymerization. Polymerization might be lower since more radicals might deactivate themselves.

Table 1. Conditions and results of the redox polymerization of NIPAM by using hydroxylated soya oil polymer in acetone (40 mL) for 60 min.

Run no.	Hydroxyl.-PSy (g)	APS (g)	NIPAM (g)	Water (mL)	Blocks in copolym. wt%[a]		Yield (g)	GPC results, $\times 10^{-3}$		
					PSy	NIPAM		Mn	Mw	1 PDI
Tpsy-N1	1.5	1.5	3	3	9.6	90.4	4.34	10.46	17.3	1.65
Tpsy-N4[b]	1	1	2	30	19.4	80.6	2.74	26.6	54.5	2.05
Tpsy-N5[c]	1	1	3	3	13.4	86.6	3.76	14.74	27.4	1.86
Tpsy-N6	0.1	0.5	2.5	3	16.9	83.1	2.58	14.0	20.2	1.44
Tpsy-N7	0.28	0.5	2.5	3	20.8	79.2	2.73	14.8	23.6	1.59
Tpsy-N8	0.65	0.5	2.5	3	13.3	86.7	2.65	13.5	22.4	1.66
Tpsy-N9	0.8	0.5	2.5	3	15.3	84.7	2.80	13.2	21.3	1.62
Tpsy-N10	1.0	0.5	2.5	3	26.8	73.2	2.97	11.7	18.0	1.54
Tpsy-N11	1.5	0.5	0.1	3	64.5	35.5	0.97	0.66	1.3	2.00
Tpsy-N12	1.5	0.5	0.25	3	49.3	50.7	1.33	0.63	1.50	2.37
Tpsy-N13	1.5	0.5	0.50	3	51.0	49.0	1.61	-	-	-
Tpsy-N14	1.5	0.5	0.75	3	36.9	63.1	1.84	-	-	-
Tpsy-N15	1.5	0.5	1.0	3	31.4	68.6	2.44	8.28	12.58	1.52

[a] calculated from ^{1}H NMR, [b] polymerization time is 90 min, [c] polymerization time is 150 min

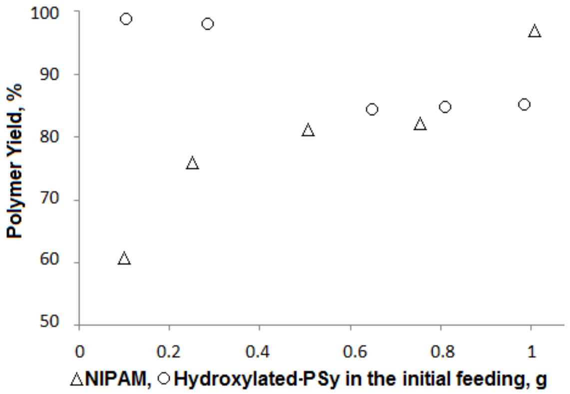


Figure 1. Percentage values of polymer yield versus the increase in the initial Δ NIPAM and ○ Hydroxylated-PSy feeding. (Δ TpsyN11, TpsyN12, TpsyN13, TpsyN14, TpsyN15 samples; ○ TpsyN6, TpsyN7, TpsyN8, TpsyN9, TpsyN10 samples).

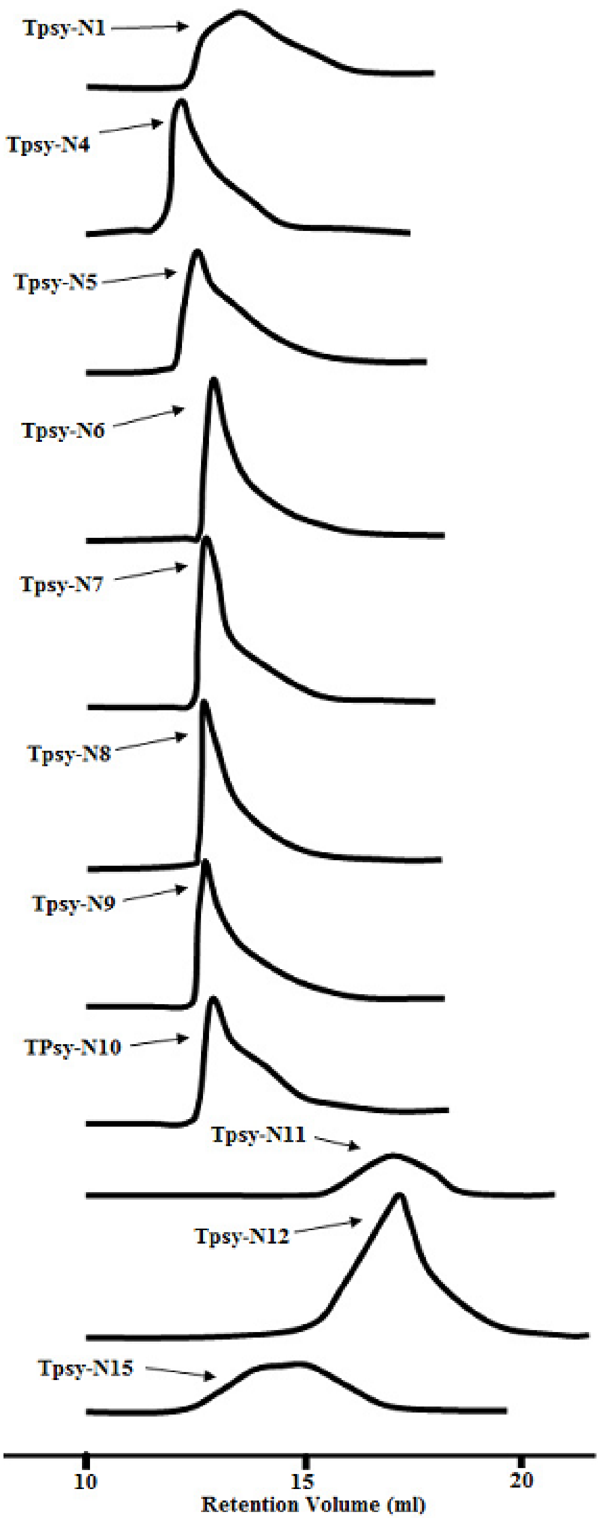


Figure 2. GPC profile hydroxylated-PSy-g-PNIPAM graft copolymers (Tpsy series in Table 1).

The variation in the polymer yield with the increasing initial feed ratio of NIPAM is given in Figure 1. It shows that the yields of the copolymer increase with the increase in the initial feed ratio of NIPAM. It gives moderate yields between 61 and 97%w/w. The percentage value of polymer yield versus hydroxylated-PSy initial feed ratio (Tpys-N6-Tpys-N10 series) is also given in Figure 1. It shows that the yields of the copolymer decrease with the increase in the initial feed ratio of hydroxylated-PSy It gives high yields between 81 and 97%w/w. Based on ^{1}H NMR, these graft copolymers included 35–90 wt% NIPAM content and were included in the initial feed ratio. Figure 2 shows GPC profiles of hydroxylated-PSy-g-PNIPAM graft copolymers. The average molecular weights (MW) of the graft copolymers are between 1.300 and 54.500 g/mol.

All synthesized graft copolymers contained characteristic signals in their proton ^{1}H NMR and FTIR spectra: the 1H NMR spectrum of the graft copolymer samples hydroxylated-PSy-g-PNIPAM included characteristic peaks, as indicated in Figure 3 (δ, ppm): –CH_2 of PSy at 3.7, 1.6, 1.4, and 0.9; the peaks at 5.3–6.0 ppm originate from the protons of the unsaturated oil segments in methylene groups of the triglyceride. The vinylic protons are determined at 5.5–6.2 ppm. In addition, the signals of protons in the PNIPAM structure are also seen in the spectra at 1.1–1.4 ppm (–CH_3), 2.0–2.2 ppm (–CH_2–), and 3.8–4.1 ppm (–CH–).

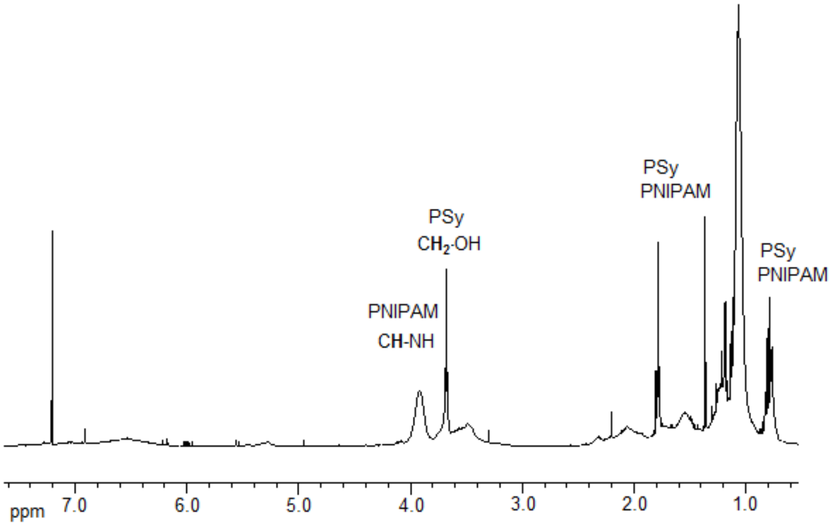


Figure 3. ^{1}H NMR spectrum of hydroxylated-PSy-g-PNIPAM graft copolymer sample (Run no: Tpsy-N10).

Figure 4 shows the FTIR spectrum of typical graft copolymers (Tpsy-N10 and Tpsy-N11 in Table 1) together with the related homopolymers. The amide groups of carbonyls signals at 1660 cm^{-1} and the –NH– group at 3320 cm^{-1} attributed to the PNIPAM row are also supported by the existence of an absorption band at 2950 cm^{-1}, characteristic of the PSy segment. The signals of the ester groups' carbonyls at 1740 cm^{-1} and the ether group at 1160 cm^{-1} are attributed to the PSy.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were also used for the thermal analysis of graft copolymers (Table 2). A DSC thermogram of the hydroxylated-PSy-g-PNIPAM graft copolymers is shown in Figure 5. Glass transition temperatures, T_g, for each sample were observed to be considerably lower than those of the PNIPAM homopolymer (Tg = 135 °C).[54] A plasticizer effect of PSy in graft copolymers was observed, indicating a lower glass transition than that of pure PNIPAM. T_g values were observed for the hydroxylated-PSy-g-PNIPAM samples for Tpsy-N1 (T_{g1} = 20 °C, T_{m1} = 84 °C), Tpsy-N4

(T_{g1} = 48 °C, T_{m1} = 107 °C, T_{m2} = 121 °C), Tpsy-N5 (T_{m1} = 84 °C), Tpsy-N6 (T_{g1} = 15 °C, T_{m1} = 84 °C), Tpsy-N7 (T_{m1} = 129 °C), Tpsy-N8 (T_{g1} = 98 °C), Tpsy-N9 (T_{g1} = 55 °C), and Tpsy-N10 (T_{g1} = 60 °C). Furthermore, a plasticizer effect of PSy was clearly observed upon insertion of the PSy blocks into the PNIPAM graft copolymers. Table 2 shows the decomposition temperatures, T_d, of the graft copolymers. They were similar to those of PNIPAM at around 431 °C.[54] The plasticizing effect of PSy blocks reduced the decomposition temperatures of PNIPAM conjugates 35 °C. The same behavior was observed in our previous research.[6,7]

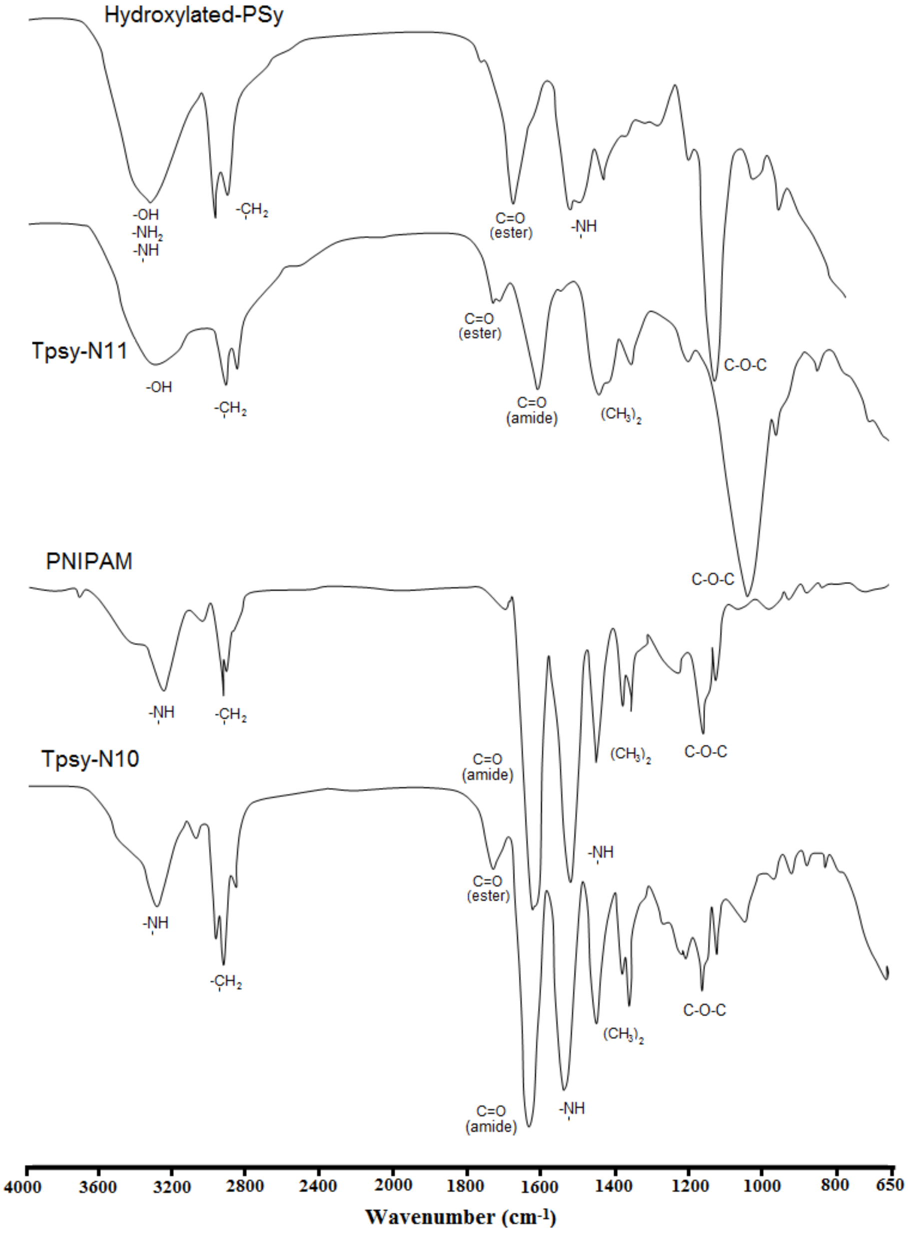


Figure 4. FT-IR spectrum of hydroxylated-PSy, PNIPAM, hydroxylated-PSy-g-PNIPAM graft copolymers (Tpsy-N10, Tpsy-N11).

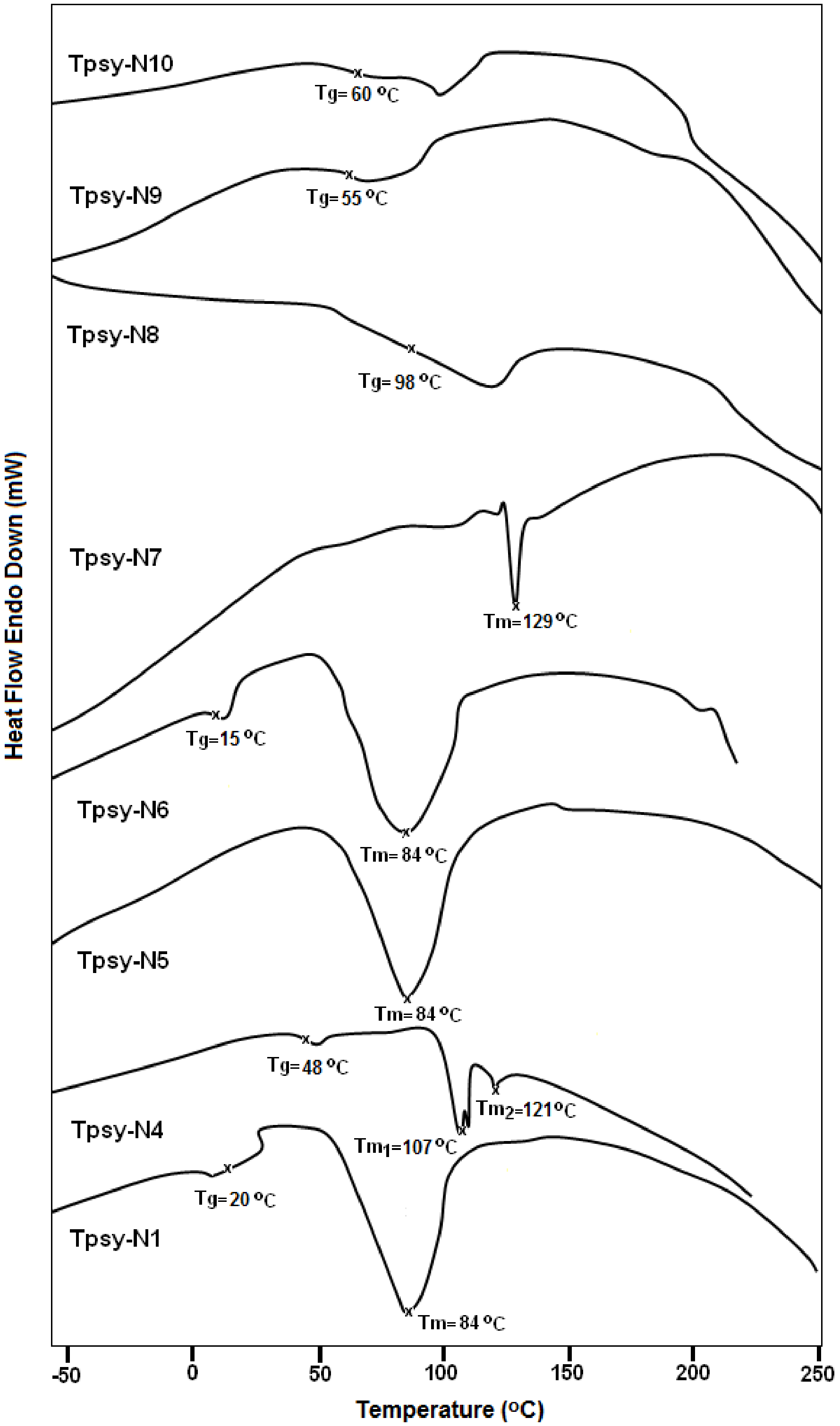


Figure 5. DSC thermogram of the hydroxylated-PSy-g-PNIPAM graft copolymers (samples: Tpsy-N1, Tpsy-N4, Tpsy-N5, Tpsy-N6, Tpsy-N7, Tpsy-N8, Tpsy-N9, Tpsy-N10, in Table 2).

Table 2. Thermal properties of the PSy, poly (N-isopropylacrylamide) (PNIPAM), and hydroxylated-PSy-g-PNIPAM graft copolymers.

Sample	DSC (°C)				TGA(°C)			
	T_{g1}	T_{g2}	T_{m1}	T_{m2}	T_{d1}	T_{d2}	T_{d3}	T_{d4}
PSy $^{(ref.8)}$	–44	–18	2	-	-	-	-	420
PNIPAM $^{(ref.54)}$	135	-	-	-	-	-	-	431
Tpsy-N1	20	-	84	-	-	180	310	390
Tpsy-N4	48	-	107	121	145	240	320	395
Tpsy-N5	-	-	84	-	130	-	330	395
Tpsy-N6	15	-	84	-	110	260	280	390
Tpsy-N7	-	-	129	-	115	300	395	550
Tpsy-N8	98	-	-	-	120	290	395	540
Tpsy-N9	55	-	-	-	105	210	395	520
Tpsy-N10	60	-	-	-	100	290	410	520

2.3. Cloud point measurements

Figure 6 shows the ordinary optical density curves for 10 wt% graft copolymer solutions as a function of heating rate.

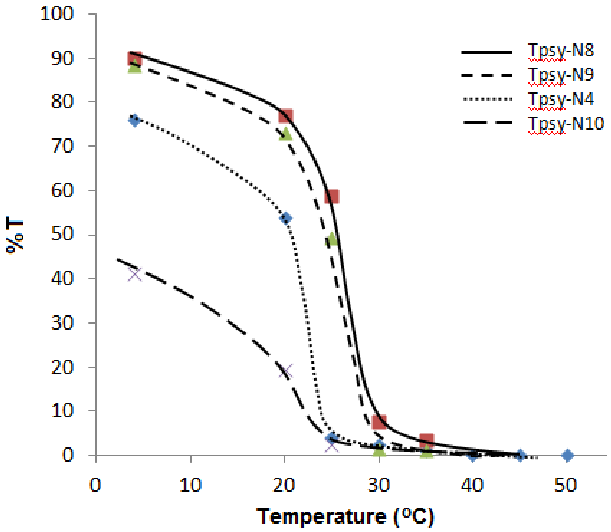


Figure 6. Temperature dependence of transmittance (%T) of hydroxylated-PSy-g-PNIPAM graft copolymers.

The diminution of UV transmittance observed upon heating was quite a sudden phenomenon, while the concomitant redissolution upon cooling at the same rate was observed to be a considerably slower process. The degree of transmittance of the copolymers was determined to be 4 °C to 50 °C. Figure 6 indicates the temperature dependence of the transmittance of PNIPAM graft copolymers. From the plots of %T versus temperature, we found the LCSTs of the copolymers to be 29 °C for Tpys-N8, 28 °C for Tpsy-N9, 23 °C Tsyp-N10, and 22 °C for Tsyp-N4, corresponding to the increasing content of the hydrophobic units (PSy). Enhanced hydrophobicity of the copolymers causes lower LCST values than the LCST value of PNIPAM homo polymer, 32 °C.[6,7]

3. Experimental part

3.1. Chemicals

Soya oil was a gift from Çotanak/Altaş Yağ, Su ve Tarım Ürünleri Gıda İnşaat Otomotiv Nakliyat San. ve Tic. A.Ş. Ordu, Turkey. It contains palmitic acid (10.7 wt%), stearic acid (4.6 wt%), oleic acid (23.5 wt%), linoleic acid (52.8 wt%), and linolenic acid (5.7 wt%). Antioxidant adduct inside the commercial soya oil was removed by leaching three times with ethanol. N-isopropylacrylamide (NIPAM; Aldrich) was purified by recrystallization from n-hexane and dried under a vacuum at room temperature. Diethanol amine, other chemicals, and the solvents were supplied by Aldrich and used without further purification.

3.2. Instrumentation

The ^{1}H NMR spectra of the graft copolymers were obtained using a Bruker Avance 400 spectrometer (400 MHz) using $CDCl_3$ as the solvent. FT-IR and FT-IR-ATR spectra were obtained using a Nicolet 520 model FT-IR and a PerkinElmer FT-IR spectrometer 100. Graft copolymers' FT-IR spectra were taken as KBr samples. UV-vis spectra were obtained using a UNicam UV2-100 spectrometer.

A gel permeation chromatography (GPC) instrument, the Viscotek GPCmax autosampler system, which consists of a pump, three ViscoGEL GPC columns (G2000HHR, G3000HHR, and G4000HHR), a Viscotek UV detector, and a Viscotek differential refractive index detector with a THF flow rate of 1.0 mL min^{-1}, was used to create GPC measurements of the polymer samples at 30 °C. PS standards with narrow molecular weight distributions were used to calibrate both detectors. Viscotek OmniSEC Omni–01 software was used to analyze the data. The Setaram differential scanning calorimetry (DSC) DSC-141 series thermal analysis system was used to carry out thermal analysis of graft copolymers under nitrogen. Generally, a dried sample was heated at a rate of 10 °C/min from 50 °C to 150 °C under N_2 atmosphere. 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.

3.3. Autoxidation of soya oil

Autoxidation of soya oil was prepared according to our previous research.[7–10] Soya oil (50 g) dispersed in a 16-cm petri dish was exposed to sunlight in air at room temperature. After 5 months, a gel polymer film formed, along with a waxy and viscous liquid. The soluble part of the polymeric soya oil (PSy) was separated from the gel via chloroform extraction for 24 h at room temperature.

3.4. Hydroxylation reactions of soya oil polymer

The hydroxylation reaction between PSy-ox and diethanol amine was performed in a round bottom flask at 90 °C for 24 h, according to the procedure mentioned in the references.[20] For example, a round bottom flask (250 mL) containing 5.0 g of PSy-ox and 5.0 mL of diethanol amine was kept in oil bath at 90 °C for 24 h. The crude product was dissolved in 20 mL of acetone. It was filtered and the hydroxylated-PSy was precipitated in 100 mL of petroleum ether. The hydroxylated-PSy was dried under a vacuum at room temperature for 24 h. Water solubility was tested in a test tube by mixing the hydroxylated-PSy (ca. 0.6 g) with distilled water (ca. 5 mL). For the solubility test in acidic solution, 0.1 N HCl was used instead of distilled water.

3.5. Synthesis of graft copolymers

Hydroxylated soybean oil and given amounts of ammonium persulfate (APS) were mixed for 15 min in a 60 °C water bath. The mixing process was carried out by adding 3 mL of distilled water in order to increase the solubility of APS, and 40 mL of acetone. Then NIPAM was added to the solution and the polymerization reaction was produced at the same temperature for 60 min. At the end of polymerization, precipitation was performed with petroleum benzene. The resulting material was separated from the solvent by decantation and dehydrated at room temperature. For purification, the material was dissolved with chloroform again and precipitation was produced with petroleum benzene. It was dehydrated at room temperature for 1 night and then was placed in a 50 °C vacuum for 1 day.

3.6. Cloud point measurements

Tubes containing hydroxylated-PSy-g-PNIPAM graft copolymer aqueous solutions were immersed in distilled water in temperatures ranging from 4 °C to 50 °C, and cloud point measurements were performed.[52,53] At each temperature, the graft copolymer solutions were drenched in distilled water for 24 h before measurements of transmittance were taken (%T). When the first opacity was visible in the solution, the cloud point was set at that temperature. A Unicam UV2-100 spectrophotometer was used to observe the optical phase transition at 500 nm.

4. Conclusions

Thermo-responsive hydroxylated-PSy-g-PNIPAM graft copolymers were successfully obtained by using APS as an initiating system. Hydroxylated-PSy samples initiated the copolymerization of NIPAM at 60 °C in acetone/water solution because of their hydroxyl groups, leading to a high yield of hydroxylated-PSy-g-PNIPAM graft copolymers. Two hydrophilic segments (hydroxylated soya oil and NIPAM) were used for the first time to synthesize hydrophilic thermo-responsive soya oil graft copolymers, and a redox aqueous polymerization system was used for the first time to synthesize hydroxylated-PSy-g-PNIPAM graft copolymers using hydroxylated soya oil. These thermo-responsive polymers show improved sensitivity towards UV transmittance behaviors and have potential field applications in new application sectors within bioengineering and other industries.

Acknowledgments

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