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Effect of 2-hydroxyethyl methacrylate content on the emulsion polymerization process of styrene–butyl acrylate–acrylic acid: Chemical, thermal and film properties of polymer latex

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Abstract
In this study, a series of hydroxyl functionalized styrene acrylate latex particles were prepared using the 2-hydroxyethyl methacrylate (HEMA) monomer as a hydroxyl source via the seeded emulsion polymerization method. The effect of anionic/nonionic surfactant on the morphology and thermal behaviors of the prepared polymer latex particle was studied. The structure and morphology of polymer latex particles were characterized using FT-IR, ^{1}H-NMR, DSC, TGA, DLS, and SEM techniques. The water-soluble HEMA monomer led to homogeneous nucleation, in addition to micellar nucleation observed due to the water-insoluble styrene and butyl acrylate monomers. The unmodified polymer latex particle had a glass transition temperature (T_g) of 7.5 °C. The T_g of hydroxyl functionalized polymer latex particle had 13.9, 14.8, 19.0, and 18.8 °C in the presence of 2.5, 4.0, 6.0, and 10.0 mass % HEMA, respectively. The average particle size was 95.30, 98.30, 115.90, 167.00, and 153.50 nm at the polymer latex content of 0, 2.5, 4.0, 6.0, and 10.0 mass % HEMA, respectively. With the addition of 1.35 mass % NP-40, the particle size of polymer latex increased from 167.00 to 218.50 nm in the presence of 0.9 mass % SLS. The addition of nonionic surfactant NP-40 affected the microstructure of polymer latex film and, consequently, its thermal characteristics.

Keywords Styrene acrylate copolymer · HEMA · Polymer latex · Functional hydroxyl · Seeded polymerization

Introduction

Due to environmental regulations, many coatings producers have preferred waterborne coatings over solvent-borne ones in recent years [1]. Polymer latex particles containing hydroxyl groups have been widely studied and used in coating systems due to the several modifications of their physical and chemical properties [2]. These polymer latexes facilitate crosslinking with polyisocyanates, epoxy resins, and amino resins, thus improving the properties of coating films. 2-Hydroxyethyl methacrylate (HEMA) is a hydroxyl-containing monomer that is a promising material for coating formulations. HEMA-containing polymer latexes have attracted much attention due to their excellent performance in waterborne coating applications; however, the chemical properties of polymer latex still need to be developed [1–3].

The addition of functional monomers such as HEMA can change the mechanical properties of the poly(HEMA-co-acrylic acid) hydrogels [1]. Some researchers have developed several polymerization modification approaches to improve the potential application of the HEMA-based films [4–7]. The density of chains is increased in the presence of HEMA, thereby improving the performance of the coating film. Mohammad Sadeghi [2] has studied the pH-responsive swelling-deswelling properties of poly(Acrylic acid-co-HEMA) grafted chitosan hydrogels and indicated that the swelling amount of the grafted hydrogels has influenced by HEMA. Ho-Nam LIM et al. [3] used HEMA as a monomer to enhance glass ionomer cement's mechanical and shear bond strength. The preparation of a superporous hydrogel is complicated due to the low solubility of the peroxy sulfate-based initiators in an aqueous solution. Omidian et al. [8] examined the effect of several variables in the preparation of superporous hydrogels based on HEMA. The superporous

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hydrogel with the HEMA group proved a good candidate as a superporous hydrogel. Zhu et al. [9] used HEMA as a functional hydroxyl monomer to prepare the waterborne acrylate/polyester emulsion having high -OH content. The crosslinking density of the polymer films increased when HEMA occupied a large proportion of the polymer. In order to avoid the problems arising from surfactants used in emulsion polymerization, some researchers studied the emulsifier-free emulsion polymerization systems with hydrophilic monomers in the absence of surfactants [10, 11]. Kang et al. [10] synthesized the poly(MMA-HEMA)/SiO2 composite particles via surfactant-free aqueous emulsion copolymerization. They used the esterification process to make polymer/silica composite from HEMA and the -OH groups on the silica surface and then copolymerized with other monomers. Zhang et al. [11] modified the nano-silica particles with a HEMA monomer. Thus, they could improve the miscibility of the silica nanoparticles and poly(methyl methacrylate-HEMA) emulsion. Typically, polyurethane acrylate is a segmented polyurethane oligomer ended with acrylic functionality, such as HEMA. Seo et al. [12] used HEMA in waterborne two-package polyurethane acrylate coatings. Santos et al. [13] studied the emulsion polymerization of HEMA in the presence of a hydrophilic monomer (acrylic acid). They found that the content in HEMA has improved cytocompatibility, hemocompatibility, and thrombogenic character. The number of hydroxyl groups on polymer latex should ensure a specific crosslinking density to obtain a stable emulsion.

The emulsion polymerization occurs in the three stages called Interval I, Interval II, and Interval III [14]. Interval I is the particle formation stage; the growth of particles defines interval II via propagation with monomers; Interval III is the final stage of polymerization. Among these stages, the nucleation stage (Interval II) plays a major role in the properties of polymer latex. After adding a water-soluble redox initiator into the aqueous phase, the hydrophilic oligomeric radicals are formed in Interval I. the oligomeric radicals precipitate and are stabilized by surfactant adsorption. This process is called homogeneous nucleation. The oligomeric radicals can also enter micelles produced by the surfactant, and this process is called micellar nucleation. The addition of hydrophilic monomers into emulsion may lead to homogenous nucleation, and as a result, more new polymer latex particles would be produced. The mechanism of polymer latex formation in the emulsion polymerization of hydrophobic monomers is different from hydrophilic monomers, on which the homogeneous nucleation mechanism is based. Homogenous nucleation has certain benefits, such as improving the particle coalescence process [15]. The core–shell morphology of the polymer latexes in emulsion polymerization did not occur when the HEMA containing polymer latex was used in the core of the polymer latex particle [15]. For this reason, preparing polymer latexes with functional groups is limited compared to that without functional groups.

The present study investigates the effect of functional hydroxyl monomers on polymer latex film properties and stabilities. The preparation and characterization of poly(styrene-co-butyl co-acrylic acid-co-hydroxyethyl methacrylate (SBA) copolymer latexes in the presence of anionic surfactants and/or a mixture of anionic and non-ionic surfactants were investigated in this study. Surfactants such as sodium lauryl sulfate (SLS) and nonyl phenoxypolyethoxyethanol (NP-40) used in water-based coatings were selected. The effects of SLS concentration, the ratio of SLS/NP-40 in the emulsions, the concentration of HEMA monomer on the particle size, film property, glass transition temperature, and thermal stability of the polymer latex were investigated. The structure of polymer latexes was characterized by Fourier transform infrared (FT-IR) and ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectroscopies and their swelling behaviors were studied with dynamic light scattering (DLS). The microstructure of particles was observed by scanning electron microscope (SEM). Differential scanning calorimetry (DSC) and minimum film-forming temperature (MFFT) were employed to measure the hardness of the polymers. The thermal stability of the polymers was determined by thermogravimetric analysis (TGA).

Experimental

Materials and instrumentation

Butyl acrylate monomer (BA, Aldrich), 2-hydroxyethyl methacrylate monomer (HEMA, Aldrich), acrylic acid monomer (AAc, Aldrich), styrene monomer (Sty, Aldrich), ammonium persulfate (APS, Aldrich), Sodium Dodecyl Sulfate (SLS, Aldrich), and sodium bicarbonate (Aldrich) were used as received. TERGITOL™ NP-40 (nonylphenol with 40 mol of ethylene oxide) was a technical-grade chemical purchased from Dow Chemical.

The chemical structure of polymer latex particles was characterized by Fourier transform infrared (FTIR) spectrometer (Spectrum 100, PerkinElmer) with attenuated reflectance (ATR) technique in the range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1}. ^{1}H-NMR spectra were recorded with an NMR spectrometer (Oxford-NMR300) using deuterated dimethyl sulfoxide (DMSO-d$_6$) as solvent. The thermal gravimetric analyses (TGA) curves were obtained by heating at 10 °C/min rate up to 1000 °C under a dry air atmosphere using EXSTAR SII TGA/DTA 7200 TG/DTG apparatus. DSC curves of the polymer latex films were obtained under a nitrogen atmosphere between -50 °C and 100 °C (10 °C/min heating rate) with Perkin Elmer DSC 6000 apparatus. Particle size and morphology of polymer latex particles were recorded using a ZEISS Supra 40 VP model field emission scanning electron microscopy (SEM). Size distribution of the polymer latex particles was measured using a Dynamic Light Scattering (DLS) instrument (MALVERN Nano-ZS Zeta Potentiometer). The calculated diameter is an intensity weighted average particle size. The detection limit of the instrument was 0.6 nm–6 mm. Minimum Film Formation Temperatures of the polymer latex particles were determined by Rhopoint MFFT 90 device.

Preparation of the polymer latex particles

The polymer latex particles were synthesized in a 1-L glass reactor fitted with a reflux condenser, Teflon stirrer, nitrogen gas inlet, thermometer, initiator solution, and monomer emulsion inlets. The reactor was loaded with water, $NaCO_3$, and surfactant (SLS/NP-40). Their amounts were 98 mass %, 0.8 mass %, and 0.9 mass % (for the polymer latex with 0.9 mass % SLS) of the total monomer amount, respectively. The reactor was heated to 80 °C with a circulating water bath by mixing with a mechanical stirrer under a nitrogen atmosphere. The amount of APS in the aqueous initiator solution was 0.4 mass % of the total monomer amount. The milky monomer emulsion was prepared by mixing water, Na_2CO_3 (0.3 mass % of monomers), surfactant, and monomers [16]. Sty, BA, AAc, and HEMA ratios of the SBA polymer latex particles prepared were given as mass % in Table 1. For seeding, 25 mass % of the initiator solution first stream was added dropwise into the mixture, including 5 mass % of the monomer emulsion. 30 min later, the emulsion was blue-colored. The feed consisted of two streams. The first was an initiator solution, and the second was a mixture of monomers. The rest of the initiator and monomer emulsion was fed to the system with a peristaltic pump in 4 h. HEMA-functionalized polymer latexes were obtained using the same experimental route [Fig. 1]. HEMA was added to the monomer emulsion at the feeding step, and in this step, the amount of HEMA was 2.5, 4.0, 6.0, and 10.0 mass % of the total monomer mass. In order to investigate the effect of surfactant amount on SBA-HEMA 6.0 polymer latex, the procedure was repeated by changing SLS to 0.9 mass %, 3.0 mass %, 6.0 mass %. Also, the effect of nonionic surfactant was examined on SBA-HEMA 6.0 polymer latex having a surfactant content of 0.9 mass % SLS /1.35 mass % NP-40. The polymer latex films were prepared by pouring polymer latex emulsion on a glass plate, and then water evaporated at room temperature.

3- Results and discussion

FT-IR and ^{1}H NMR studies

The FTIR spectra of prepared polymer latex particles are given in Fig. 2. The characteristic stretching band of the carbonyl -C=O groups in the polymer chain appeared at 1727 cm^{-1}. The bands at 2958 cm^{-1} and 2875 cm^{-1} belong to aliphatic C-H stretching vibrations. Observation of the

Table 1 Recipes for preparation of SBA latex particles

Latex	BA/mass %	Sty/mass %	AAc/mass %	HEMA/mass %
SBA	54	44	2	0
SBA-HEMA 2.5	52.5	43	2	2.5
SBA-HEMA 4.0	51.5	42.5	2	4.0
SBA-HEMA 6.0	50.5	41.5	2	6.0
SBA-HEMA 10.0	48	40	2	10.0

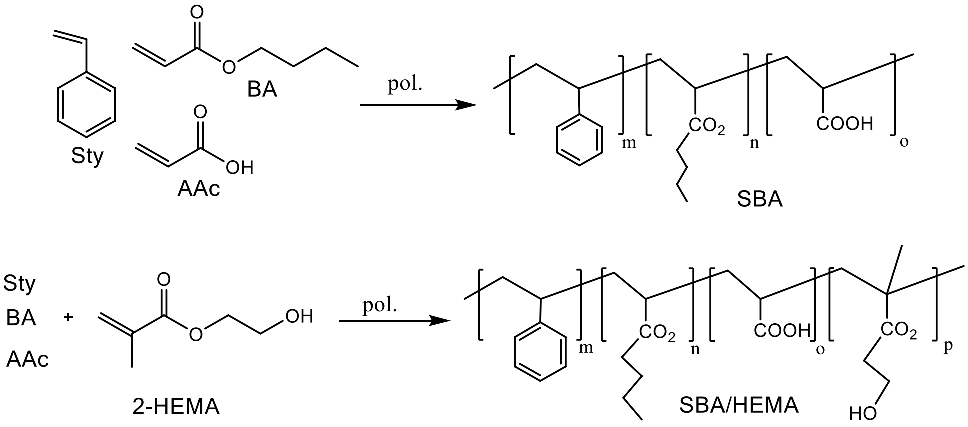
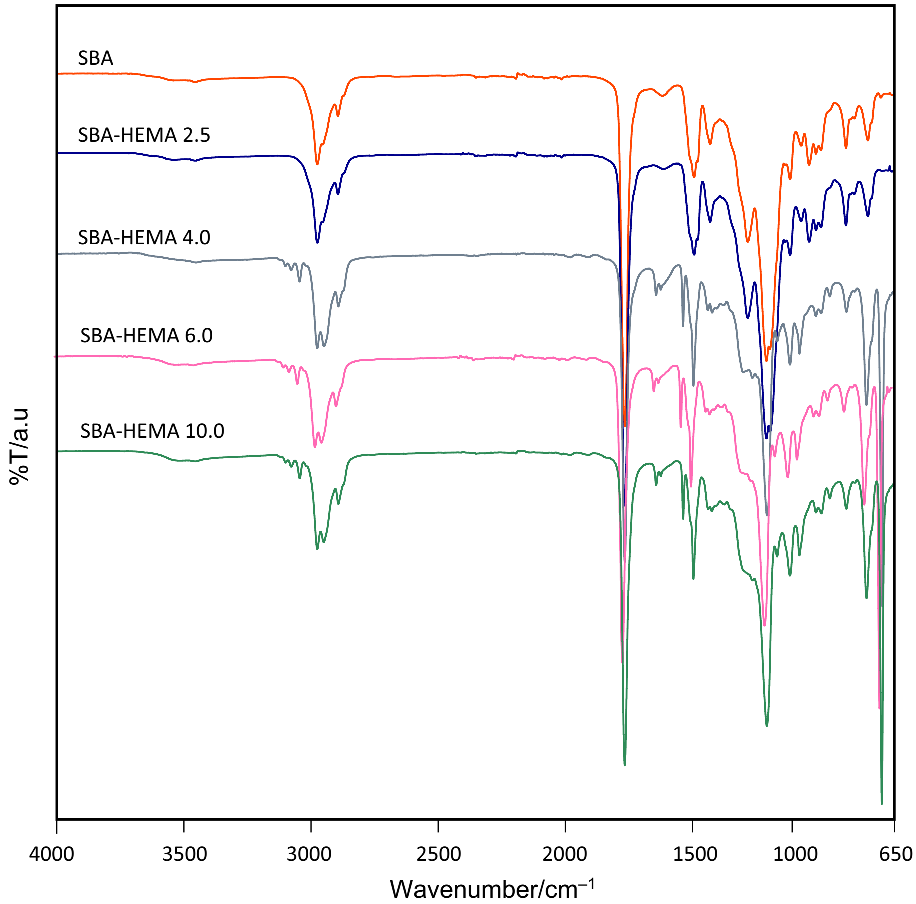


Fig. 1 Preparation of HEMA-functionalized styrene/butyl acrylate/acrylic acid (SBA) polymer latex

Fig. 2 FTIR spectra of SBA latex having different amounts of HEMA moiety



bands at 3028 cm^{-1} and 1494, 1453 cm^{-1} proves the styrene moiety in the polymer chain. The bands at 1160 cm^{-1} and 1066 cm^{-1} are the ester stretching bands showing -C–O–C- [17]. Unlike the spectrum of SBA polymer latex, in all HEMA-containing polymer latexes, the bands occurred at 3510 cm^{-1} and 3444 cm^{-1}, corresponding to the free and associated OH stretching vibrations, indicating that the HEMA is in the polymer chain. ^{1}H-NMR spectra of the SBA-HEMA 6.0 polymer latex film are shown in Fig. 3. Styrene's aromatic protons in the polymer chain were observed as a large singlet at 6.74 ppm. The signals at 3.25 and 2.94 ppm belong to the methylene protons marked as d, n, and o at the BA and HEMA moieties. The CH protons e and k appeared as singlet signal at 2.09 ppm. Additionally, the multiplet signals between 0.45 and 1.05 ppm should arise from the remaining shielded aliphatic CH_3, CH_2, and CH protons at the polymer backbone [17].

DSC studies

The results indicated that the glass transition temperature (T_g) was 7.5, 13.9, 14.8, 19.0, and 18.8 °C for the polymer SBA, SBA-HEMA 2.5, SBA-HEMA 4.0, SBA-HEMA 6.0, and SBA-HEMA 10.0, respectively [Fig. 4]. The T_g increased with increasing HEMA content in polymer chain (Table 2). The higher T_g values for HEMA functionalized polymer compared to unmodified polymer can be attributed to the copolymer's increased molar mass and the reduction of copolymer chains' molecular mobility [16]. This is likely a result of the homogeneous nucleation formed by the water-soluble HEMA monomer in the emulsion. The concentrations of Sty and BA in the aqueous phase are lower than that of HEMA due to their lower water solubility than HEMA (solubilities in 100 mL water: 81, 0.03, and 0.2 g for HEMA, Sty, and BA, respectively) [15]. Thus, the amount of HEMA in the water medium becomes higher than that of Sty and BA. Hidalgo et al. [18] showed that increasing the content of water-soluble monomer leads to homogenous nucleation in the emulsion during Interval II, and the functional hydrophilic monomer precipitated from aqueous solution as a separate phase. The higher content of the hydroxyl group in polymer chains formed stronger hydrogen bonding between hydroxyl groups, which caused the observed increase in T_g [19].

As is seen from Table 3, the T_g values slightly decreased with the increasing percent of SLS. The T_g of SBA-HEMA 6.0 polymer with 0.9 mass %, 3.0 mass %, and 6.0 mass % SLS was 19.0, 18.7, and 18.0 °C, respectively. This is

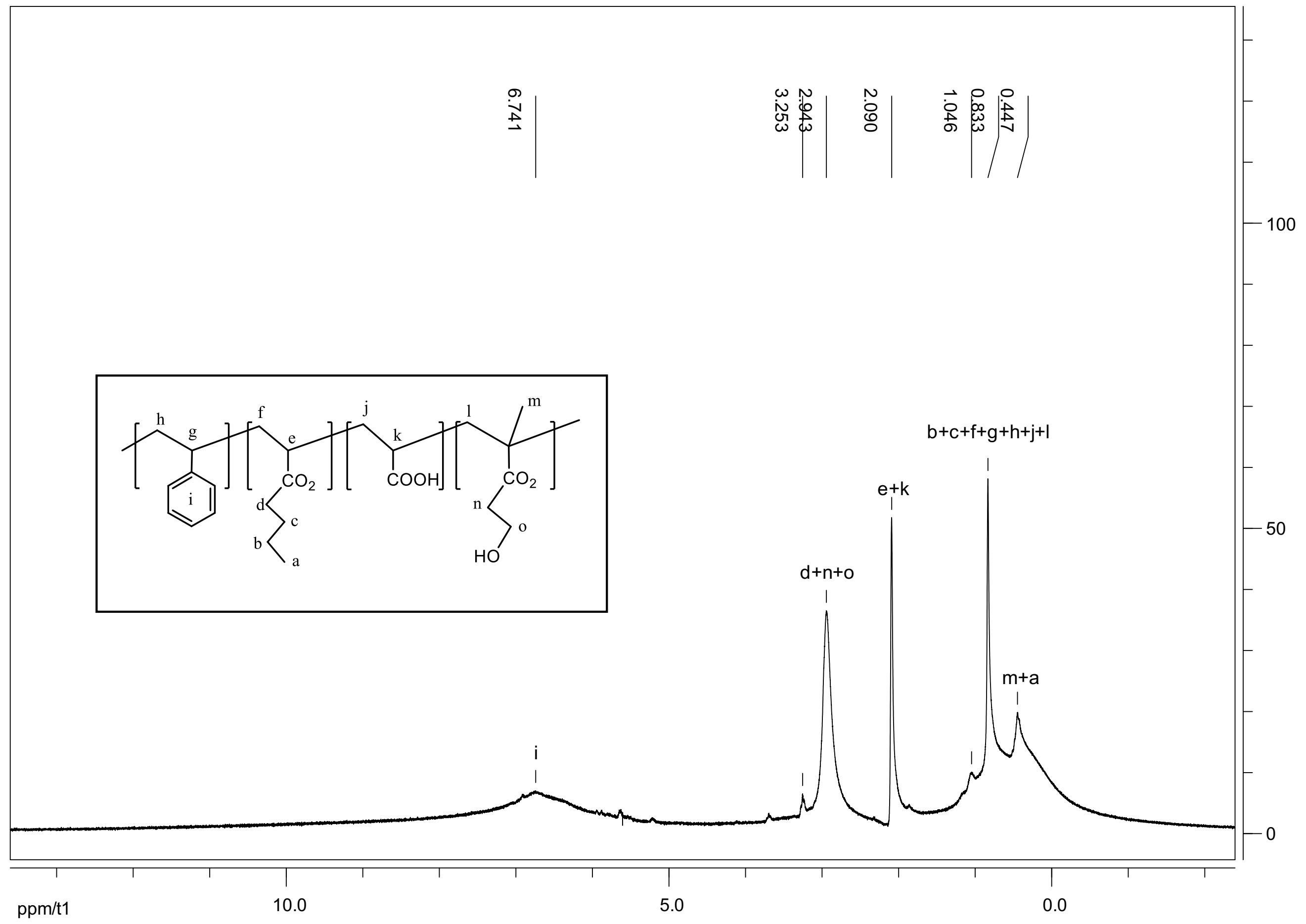


Fig. 3 ^{1}H-NMR spectrum of the SBA-HEMA 6.0 polymer film in DMSO-*d*6

likely a result of plasticization accompanying the addition of SLS. The effect of surfactant amount on the DSC curves of SBA-HEMA 6.0 polymer is presented in Fig. 5. It can be seen a second broad heat transition region in the temperature range of 60 and 80 °C, especially at the higher SLS amounts. It is known that the formation of hydrophilic oligomeric radicals is observed in the initiation step during emulsion polymerizations [15]. HEMA-rich oligomeric radicals were stabilized by surfactant adsorption and formed the new particles. T_g of the SBA-HEMA 6.0 polymer in the presence of NP-40 was only 12.9 °C. This result indicated that NP-40 nonionic surfactant played the role of plasticizer for the hydroxyl functionalized polymer, reducing T_g compared to SLS-added samples.

MFFT studies

As given in Table 2, the amount of HEMA in the polymer latex also influenced the prepared polymer latex film's minimum film formation temperature (MFFT). The MFFT values enhanced with the increasing content of HEMA. The MFFT values of the polymer latex having HEMA contents from 2.5 up to 10% by mass were found in the range of 3.3 and 6.6 °C. The content of HEMA in the copolymer chains influences the copolymer hardness/softness properties and thus the film formation. This result is reasonable that the polymer with a higher T_g value tends to have a higher MFFT value since polymer chain movement is necessary for coalescence [20, 21]. As shown in Table 3, the MFFT values decreased with increasing SLS content in SBA-HEMA 6.0 polymer latex particle. Also, the results indicated that the MFFT value obtained in the SLS/NP-40 system for SBA-HEMA 6.0 particle was much smaller than that in the SLS system. The SBA-HEMA 6.0 polymer latex has the MFFT of 3.2 °C at the surfactant content of 0.9 mass % SLS /1.35 mass % NP-40. The hydroxyl groups on hydroxyl functionalized polymer latex can form hydrogen bonds with the hydroxyl group on nonyl. They can also enter between the HEMA chains matrix during the emulsion solution transforming into the dried film [20, 21]. This led to a decrease in MFFT in the polymer latex matrix.

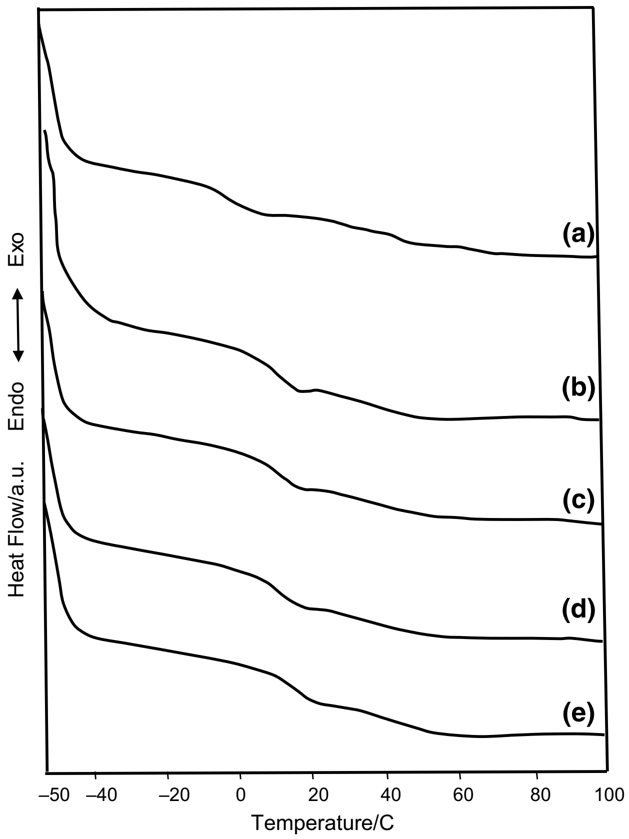


Fig. 4 **a** The effect of HEMA content on the DSC curves of SBA polymer; **a** 0 mass %, **b** 2.5 mass %, (c) 4.0 mass %, (d) 6.0 mass %, and (d) 10.0 mass % HEMA

Table 2 T_g and MFFT values for SBA polymer latex particles having different HEMA amounts

Latex	T_g/°C	MFFT/°C
SBA	7.5	3.0
SBA-HEMA 2.5	13.9	3.3
SBA-HEMA 4.0	14.8	3.7
SBA-HEMA 6.0	19.0	5.5
SBA-HEMA 10.0	18.8	6.6

Table 3 The effect of surfactant amount on the T_g and MFFT values of the SBA-HEMA 6.0 polymer

Surfactant content	T_g/°C	MFFT/°C
0.9 mass % SLS	19.0	5.5
3.0 mass % SLS	18.7	4.6
6.0 mass % SLS	18.0	2.0
0.9 mass % SLS /1.35 mass % NP-40	12.9	3.2

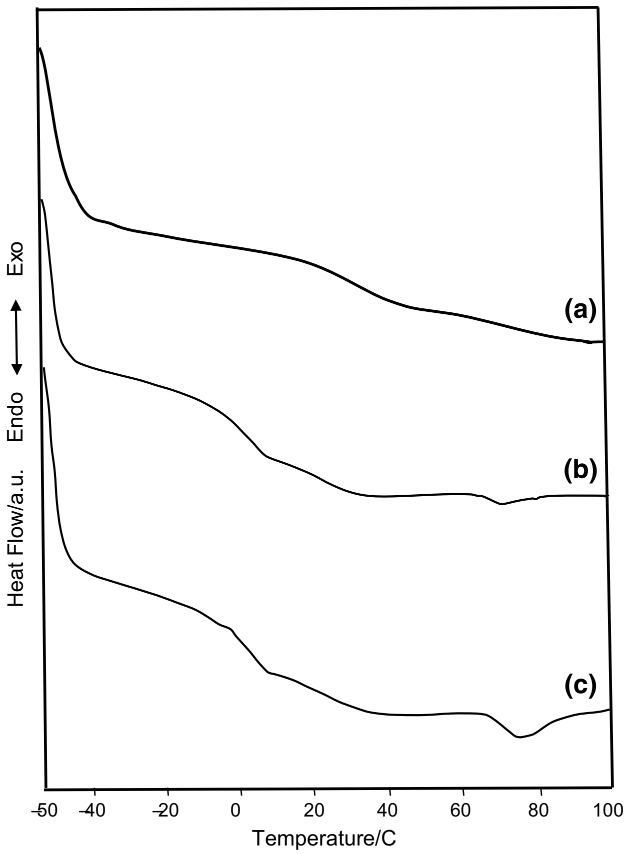


Fig. 5 The effect of surfactant amount on the DSC curves of SBA-HEMA 6.0 polymer; **a** 0.9 mass %, **b** 3.0 mass %, and **c** 6.0 mass % SLS

TGA studies

Thermal analyses of the polymer latexes were carried out under a dry air atmosphere to evaluate their relative thermal stability (Fig. 6). The results are given in Table 4. TGA analysis of samples showed three steps of mass loss. From TGA curves, the following data were obtained: (a) $T_{50\%}$, the temperature at which 50 mass % degradation occurred, (b) $T_{\max1,}$ $T_{\max2,}$ and $T_{\max3}$ are the temperatures at which the maximum rate of decomposition occurred in the first, second and third steps, respectively. In the first degradation step, the initial mass loss of 1–5 mass % occurred up to 150 °C due to the removal of the absorbed water. The thermal stability of polymer was determined from second step mass loss in the TGA curves. The $T_{\max2}$ for SBA was 371 °C. For SBA-HEMA polymers, $T_{\max2}$ increased to 403 °C by increasing the HEMA content from 0 mass % to 10 mass %. The behavior of $T_{50\%}$ versus HEMA content was similar to that observed for $T_{\max2.}$ These results proved that the addition of HEMA into the emulsion increased the thermal stability of the polymer [22–24]. The presence of a single peak in the second degradation step indicated the homogeneity of the samples

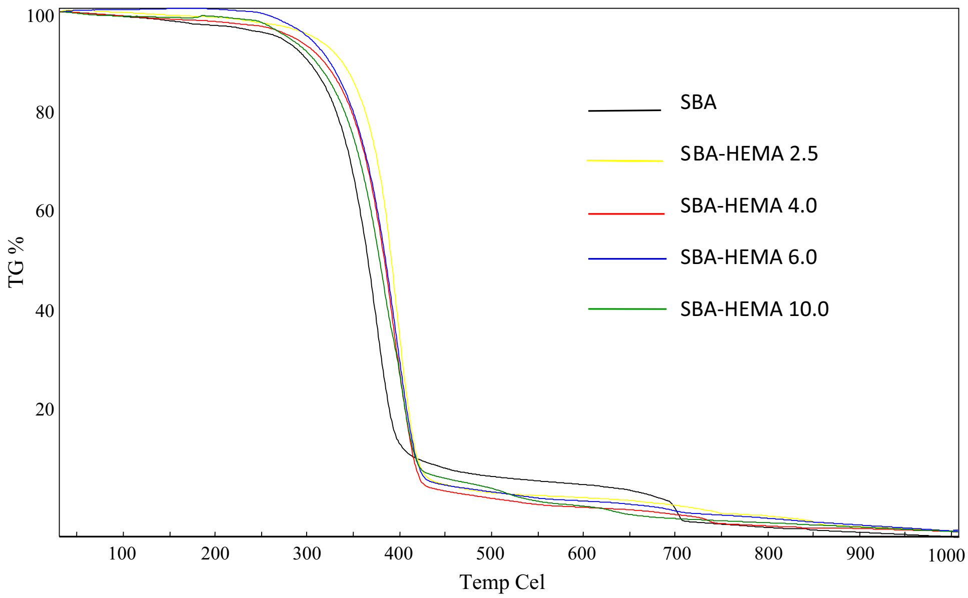


Fig. 6 TGA characteristics for polymer with different HEMA monomer amounts

Table 4 The effect of HEMA content on the thermal properties of SBA polymer

Latex	Thermal degradation step	T_{max}/°C	$(dw/dt)_{max}$/% min^{-1}	$T_{50\%}$/°C
SBA	I	100	0.26	366
	II	371	15.29	
	III	699	4.27	
SBA-HEMA 2.5	I	106	0.15	392
	II	396	14.91	
	III	849	0.63	
SBA-HEMA 4.0	I	97	0.15	385
	II	394	14.82	
	III	737	0.79	
SBA-HEMA 6.0	I	–	–	386
	II	398	14.03	
	III	695	0.45	
SBA-HEMA 10.0	I	55	0.20	378
	II	403	12.27	
	III	629	0.50	

Table 5 The effect of the surfactant amount on the thermal behavior of SBA-HEMA 6.0 polymer

Surfactant content	Thermal degradation step	T_{max}/°C	$(dw/dt)_{max}$/ % min^{-1}	$T_{50\%}$/°C
0.9 mass % SLS	I	–	–	386
	II	398	14.03	
	III	695	0.45	
3.0 mass % SLS	I	62	0.19	364
	II	375 (256^{sh})	11.05	
	III	511	1.33	
6.0 mass % SLS	I	52	0.34	359
	II	375 (242^{sh})	9.24	
	III	509	0.65	
0.9 mass % SLS /1.35 mass% NP-40	I	51	0.27	378
	II	392	11.68	
	III	731	0.77	

(see supplementary information file, Figs. S1 and S2). The kinetics of the thermal degradation steps were also studied to understand the degradation mechanism of the hydroxyl functionalized polymer. The value of $(dw/dt)_{max2}$ for the SBA polymer was 15.29%/min, and this value decreased to 12.27%/min with increasing HEMA content to 10 mass %. This result is compatible with the enhanced thermal stability with the increase in HEMA content.

In order to determine the effect of surfactant amount on the thermal stability of polymer, a series of SBA-HEMA 6.0 polymers prepared with different surfactant amounts were characterized by TGA (Table 5). In terms of T_{max2} and $T_{50\%}$, increasing the amount of anionic surfactant SLS from 0.9 mass % to 6.0 mass % reduced the thermal stability of SBA-HEMA 6.0 polymer by an average of 23–27 °C. The SBA-HEMA 6.0 polymer had the $T_{50\%}$ of 386 °C at the emulsion content of 0.9 mass % SLS, but the value of $T_{50\%}$ dropped to 359 °C for that of 6.0 mass % SLS. As shown in Fig. 7, the TGA curves for SBA-HEMA 6.0 polymer having 3.0 mass % and 6.0 mass % SLS showed a shoulder in the second decomposition step (shoulders at 256 °C and 242 °C), corresponding to the decomposition of SLS [22, 25, 26]. The TGA measurements showed that the addition of the NP-40 surfactant decreased the thermal stability of the polymer. For example, the $T_{50\%}$ of SBA-HEMA 6.0 polymer prepared

Fig. 7 The effect of surfactant amount on the TGA curves of SBA-HEMA 6.0 polymer

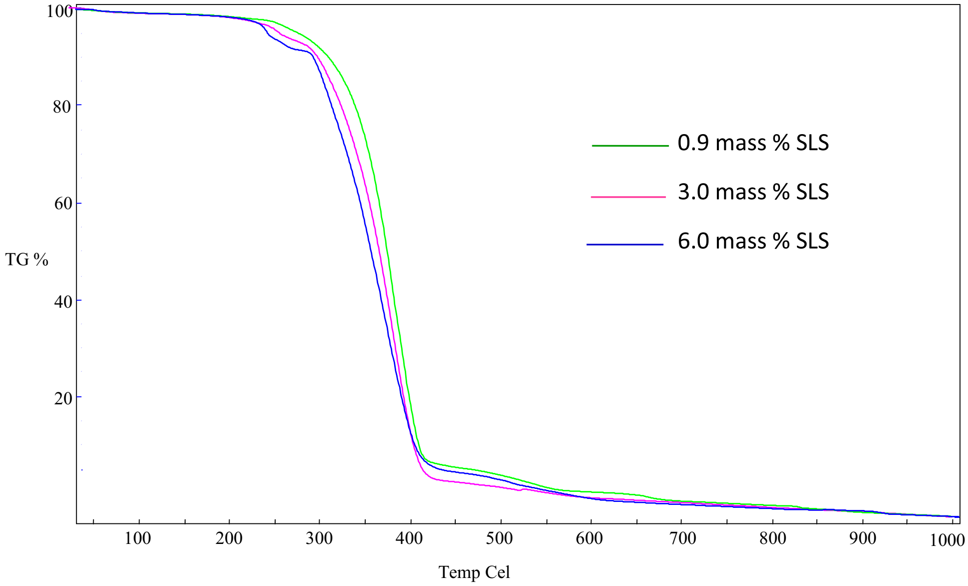


Table 6 The effect of HEMA amount on the average particle size value of the SBA latex

Latex	Average particle size/nm		
	SEM	DLS	PDI
SBA	80	95.30	0.150
SBA-HEMA 2.5	80	98.30	0.103
SBA-HEMA 4.0	108	115.90	0.090
SBA-HEMA 6.0	162	167.00	0.057
SBA-HEMA 10.0	150	153.50	0.076

Table 7 The effect of surfactant amount on the average particle size value of the SBA-HEMA 6.0

Surfactant content	Average particle size/nm	PDI
0.9 mass % SLS	167.00	0.057
3.0 mass % SLS	105.30	0.216
6.0 mass % SLS	63.29	0.226
0.9 mass % SLS /1.35 mass % NP-40	218.50	0.238

with 0.9 mass % SLS decreased from 386 to 378 °C in the presence of nonionic surfactant NP-40. Edelhauser et al. [27] reported that sodium decyl sulfate and sodium dodecylbenzene penetrate the interior of polyvinyl acetate. Vijayendran et al. [28] found that sodium decyl sulfate surfactant is first stabilized by adsorption on polyvinyl acetate polymer latex surfaces and then enters into the polymer chains. In this study, NP-40 molecules first adsorb on the surface of polymer and penetrate the interior of the polymer when the emulsion is transformed into the dried film. This led to a decrease in the thermal stability of the polymer sample. However, the polymer and SLS interaction are much poorer than between polymer and NP-40 [29].

Particle size studies

The average particle size increased from 95.30 nm to 153.50 nm for HEMA percent of 0 and 10.0, respectively (Table 6). It was reported that the -OH and acrylate functional groups of HEMA tend to swell in water [30]. The particle size of hydroxyl functionalized polymer latex particles was increased with increasing HEMA content of the polymer latex due to increased swelling of polymer latex particles. The PDI decreased from 0.150 to 0.057 in the studied HEMA concentration range. Considering PDI of all the polymer latexes were less than 0.150, it can be concluded that the HEMA-rich oligomeric radicals caused a narrow particle size distribution and good dispersibility. The HEMA monomers are more prone to react with other HEMA monomers than with styrene and butyl acrylate monomers present in the emulsion.

The average particle size decreased from 167.00 nm to 63.29 nm with the increase in SLS amounts from 0.9 to 6.0 mass % for SBA-HEMA 6.0 polymer latex. Thus, the decreased particle size with increasing SLS concentration resulted from the increased emulsion stability.

In Table 7, PDI of the polymer latex particles showed an increase with SLS up to 3.0 mass %, after which it stayed nearly constant. The increase in PDI with the addition of SLS was due to more SLS adsorbed on polymer latex particle surfaces. This may be attributed to electrostatic repulsion between negative charged SLS on polymer latex particle and OH groups on HEMA monomer. HEMA monomers in the

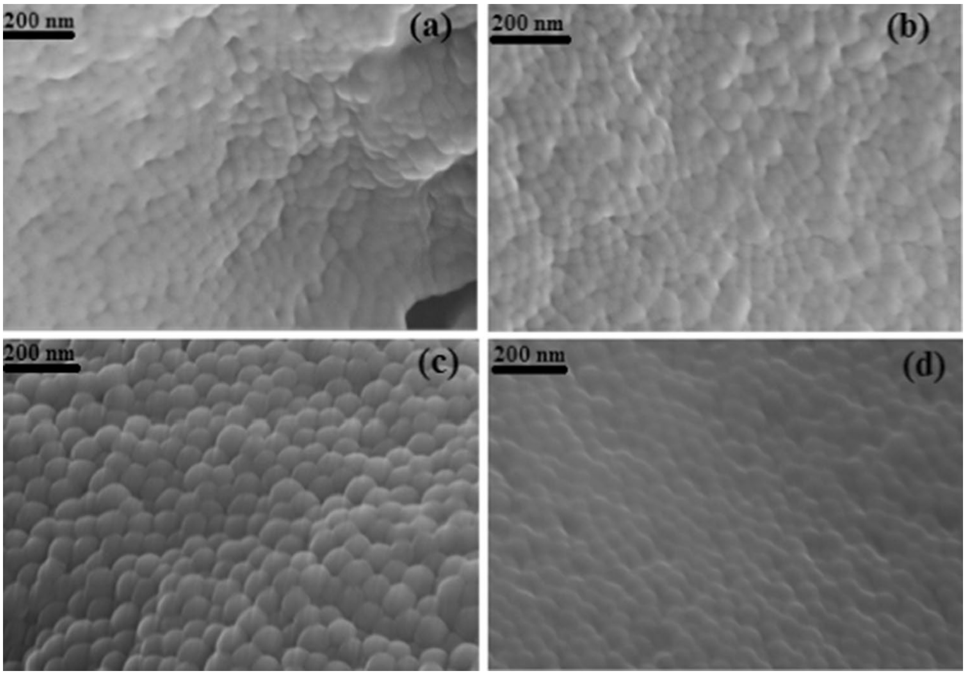


Fig. 8 SEM images of SBA polymer latex particles polymerized with **a** 2.5 mass %, **b** 4.0 mass %, **c** 6.0 mass %, and **d** 10.0 mass % HEMA

water phase are difficultly diffused into the polymer particles, leading to the second nucleation. The electrostatic repulsion led to a higher degree of heterogeneity in the final product. When the HEMA-rich oligomeric species in the aqueous phase reach a specific chain length, they precipitate from the solution. The SLS surfactant molecules maintain a saturated monolayer of adsorbed emulsifiers on the surface of the polymer latex particle. During copolymerization of HEMA monomers, particle formation occurred via precipitation of oligomeric radicals in the aqueous phase. Similarly, previous studies on the copolymerization of HEMA in water have shown new particle formation during reaction [15, 31]. These new particles will compete with the seed particles for Sty, BA, and HEMA monomers.

As given in Table 7, the particle size of polymer latex increased in the presence of nonionic surfactant NP-40. The addition of NP-40 significantly improved the particle size of polymer latex, and the particle size reached 218.50 nm at the polymer latex amount of 1.35 mass % NP-40 with 0.9 mass % SLS. The PDI increase supported the homogeneous nucleation in the presence of NP-40. For example, the PDI of emulsion is 0.057 without NP-40. On the other hand, with 1.35 mass % NP-40, the PDI increased to 0.238.

The obtained polymer latex particles were investigated with SEM (Fig. 8). SEM micrographs showed the spherical nature of the polymer latex particles. Also, the spherical structure is not changed due to an increase in the amount of HEMA in the emulsion. The SEM micrographs of SBA polymer latex in Fig. 8 show that the polymer particles kept their spherical shapes and smooth surfaces with the increased amount of HEMA in the polymer chain. There are no space between the polymer latex particles, indicating that a relatively stronger interaction between them. The SEM observation results agreed with DLS particle analysis (Table 6). In some cases, SEM images displayed smaller particle sizes than those in DLS due to polymer film formation [22].

Conclusions

The waterborne hydroxyl-functionalized polymer latexes were prepared by a two-step emulsion polymerization. The T_g values are 7.5, 13.9, 14.8, 19.0, and 18.8 °C for the polymer latex SBA, SBA-HEMA 2.5, SBA-HEMA 4.0, SBA-HEMA 6.0, and SBA-HEMA 10.0, respectively. Thermal stability was enhanced by increasing HEMA content from 0 to 10.0 mass %. Due to higher particle swelling, the polymer latex particle size was increased parallel with the amount of HEMA monomer. This is due to the plasticizing effect of water and surfactants available in the polymer latex during particle coalescence. HEMA monomers caused the formation of new particles via homogeneous nucleation in the emulsion polymerization process. The PDI value increased from 0.057 to 0.238 with the increasing amount of NP-40 from 0 and 1.35 mass % in the emulsion. The PDI increase supported the homogeneous nucleation in the presence of NP-40. The addition of nonionic surfactant NP-40 affected the microstructure of polymer latex film and, consequently, its thermal characteristics. The $T_{50\%}$ value for nonionic surfactant NP-40-added polymer latex is 8 °C lower than for anionic surfactant SLS-added polymer latex. The decrease in the thermal stability showed that NP-40 penetrates the polymer latex. The MFFT values for polymer latexes are lower than their respective T_g's. As the HEMA monomer content increased, the T_g shifted from 7.5 °C to 19.0 °C. T_g values are 100 °C and 101.85 °C for the homopolymer of Sty and HEMA monomers, respectively. The influence of amounts of the two monomers on the polymer rigidity is similar due to similar T_g values of their homopolymers. Thus, the observed increase in T_g value is due to the rise in the number of hydrogen bonds formed by the hydroxyl functional group HEMA. The SEM micrographs of SBA polymer latex showed that the polymer particles kept their spherical shapes and smooth surfaces with the increased amount of HEMA in the polymer chain. There is no space between the polymer latex particles, indicating a relatively stronger interaction between them.

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Authors' Contributions Bilge EREN designed and directed the project. Hulya ÇINAR performed the experiments. Beyhan ERDOĞAN performed the polymer latex characterization. Bilge EREN processed the experimental data, performed the analysis, drafted the manuscript, and designed the figures.

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