Hyperbranched Homo and Thermoresponsive Graft Copolymers by Using ATRP-Macromonomer Initiators

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ABSTRACT: Macromonomer initiators behave as macro cross-linkers, macro initiators, and macromonomers to obtain branched and cross-linked block/graft copolymers. A series of new macromonomer initiators for atom transfer radical polymerization (MIM-ATRP) based on polyethylene glycol (M_n = 495D, 2203D, and 4203D) (PEG) were synthesized by the reaction of the hydroxyl end of mono-methacryloyl polyethylene glycol with 2-bromo propanoyl chloride, leading to methacryloyl polyethylene glycol 2-bromo propanoyl ester. Poly (ethylene glycol) functionalized with methacrylate at one end was reacted with 2-bromopropionyl chloride to form a macromonomeric initiator for ATRP. ATRP was found to be a more controllable polymerization method than conventional free radical polymerization in view of fewer cross-linked polymers and highly branched polymers produced from macromonomer initiators as well. In another scenario, ATRP of *N*-isopropylacrylamide (NIPAM) was initiated by MIM-ATRP to obtain PEG-b-PNIPAM branched block/graft copolymers. Thermal analysis, FTIR, ^{1}H NMR, TEM, and SEM techniques were used in the characterization of the products. They had a thermo-responsive character and exhibited volume phase transition at $\sim$ 36°C. A plasticizer effect of PEG in graft copolymers was also observed, indicating a lower glass transition temperature than that of pure PNIPAM. Homo and copolymerization kinetics were also evaluated. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 536–548, 2012

Key words: atom transfer radical polymerization (ATRP); graft copolymers; hyperbranched; stimuli-sensitive polymers

INTRODUCTION

Macromonomer initiators (macroinimers), (MIMs), are polymers with a polymerizable group (e.g., methacryloyl group) at one end and an initiating group (azo or peroxide group) at the other that behaves as a macro cross-linker, macro initiator, and macromonomer to obtain highly branched and/or cross-linked block/graft copolymers in one-pot synthesis.[1,2] In conventional free radical polymerization, vinyl polymerization initiated by macroinimers has been well documented.[3–7] Bulk polymerization and copolymerization of MIMs with styrene have been compared with polymerizations mediated by macro cross-linkers (MCRs) at constant polymerization time and temperature with various initial concentrations of MIM and MCR.[8] Macroinimer concentration and polymerization time are effective on polymers obtained, from highly branched to cross-linked. Macromer initiators offer very interesting alternatives not only as initiators but also as sole surfactants or additional surfactants for miniemulsion polymerization.[9–12]

The introduction of branching into a polymer can dramatically alter its properties, so preparation of these types of macromolecules is of interest to the polymer/materials community. A recent subject in polymer/materials synthesis is the preparation of hyper branched polymers via self-condensing vinyl polymerizations (SCVP). Frechet et al. in 1995[13] reported the SCVP of AB*-monomers wherein the A-unit was the initiating group and the B*-unit was the vinyl group.

Atom transfer radical polymerization employs atom transfer from an organic halide to a transition-metal complex to generate reacting radicals, followed by transfer from the transition metal to a product radical to form the final product. Controlled living free-radical polymerization allows the controlled polymerization of a wide variety of vinyl monomers to obtain polymers with diverse, well-defined architectures.[14–20] A first report by Frechet in 1995 significantly broadened the chemistry of hyper branched polymers that allowed the use of vinyl monomers, and it was quickly expanded to different chain growth reactions, including conventional free radical

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polymerization and controlled living free radical polymerization.[21–36] Free radical polymerization is more representative for conventional, uncontrolled method. Moreover, today it is known that ATRP is controlled method of radical polymerization with pseudoliving character because of the occurrence of some small amounts of side reactions, which are not possible to be minimized especially in case of the synthesis of branched polymers.

Poly (*N*-isopropylacrylamide) (PNIPAM) gel is a well-known temperature-sensitive gel exhibiting volume phase transition at approximately its lower critical solution temperature (LCST) of 32°C. Interest in stimuli-responsive polymers has exponentially increased because of their promising potential in a variety of applications in biomedical fields.[37–40] Conjugation of PNIPAM is also a useful way to overcome certain limitations and to combine the advantageous properties of the individual components.[41–50]

In this article, we report the synthesis and evaluation of self-condensing homo-polymerization and novel thermo-responsive PNIPAM graft copolymers by the polymerization of NIPAM initiated by new PEG-based ATRP macromonomer initiators, leading to a mixture of hyper-branched PEG and formation of PEG-g-PNIPAM thermo-responsive graft copolymers, via ATRP using the CuBr/ligand catalyst system. These responsive polymers show improved sensitivity of swelling behaviors and have potential field applications in a new sector of industry and bioengineering. In addition, we have demonstrated that graft copolymers can form micelles with nonsolvated cores, comprising either the PEG block or the PNIPAM block in aqueous media.

EXPERIMENTAL SECTION

Materials

Poly(ethylene glycol mono-methacrylate) (v-PEG360-OH), PEG-2000, PEG-4000, methacryloyl chloride, CuBr, and 2-bromopropanoyl bromide were received from Sigma-Aldrich and used without further purification. CuBr (98%) was purified by stirring overnight in acetic acid. After filtration it was washed with ethanol, ether, and then dried under vacuum at room temperature. *N*-isopropylacrylamide (NIPAM) was supplied from Sigma-Aldrich and purified by means of recrystallization from n-hexane and then dried under vacuum at room temperature. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), dichloromethane (DCM), triethylamine (TEA), and toluene were received from Sigma-Aldrich and distilled under atmospheric pressure. All other chemicals were of analytical grade and used without further purification.

SYNTHESIS OF MIM-ATRPs (M495, M2203, AND M4203)

M495

A 38.87 g (73.9 mmol) of v-PEG360-OH in 30 mL of dry DCM was mixed with 9.11 g (90 mmol) of TEA. The solution was transferred into a 250-mL schlenk flask, dropping funnel, gas inlet/outlet, and magnetic stirrer. After cooling to 0°C, 20.69 g (90 mmol) of 2-bromopropanoyl bromide in 30 mL of DCM was added dropwise to the mixture of PEG and TEA. The mixture was stirred for 1 h at 0°C followed by stirring at room temperature for 24 h. The solution was filtered. Solvent was then removed by a rotary evaporator and the v-PEG-Br-360 (code: M495), MIM-ATRP was precipitated in cold diethyl ether. The product was dissolved in absolute ethanol and kept in a refrigerator overnight to be precipitated triethylamin hydrochloride crystals completely. The macromonomer initiator was then filtered, washed with cold diethyl ether, and dried under vacuum at room temperature. The pure macromer initiator was kept in a refrigerator until use.

M2203 and M4203

PEG2000 and PEG4000 were used for the synthesis of the macromonomer initiators, v-PEG-Br-2000 (code: M2203) and v-PEG-Br-4000 (code: M4203). Briefly, 18.0 g (9.0 mmol) of PEG2000 (or 36 g, 9.0 mmol of PEG4000) in 30 mL of dry DCM was mixed with 0.911 g (9 mmol) of TEA. The solution was transferred into a 250-mL schlenk flask, dropping funnel, gas inlet/outlet, and magnetic stirrer. After cooling to 0°C, 1.04 g (4.6 mmol) of 2-bromopropanoyl bromide in 30 mL of DCM was added dropwise to this solution. The solution was stirred for 1 h at 0°C. To this solution was added dropwise 30 mL of DCM solution containing 0.46 g (0.45 mmol) of methacryloyl chloride by stirring at 0°C for 1 h more. The solution was left overnight by stirring and then filtered. The solvent from the clear solution was removed by a rotary evaporator, and the macromonomer initiator was precipitated in cold diethyl ether. The product was dissolved in absolute ethanol and kept in a refrigerator overnight to be precipitated triethylamin hydrochloride crystals completely. The solution of the macromonomer initiator was filtered, washed with cold diethyl ether, and dried under vacuum at room temperature. The pure macromer initiators were kept in a refrigerator until use.

Self-initiated polymerization of MIM-ATRPs

In the self-initiated ATRP process, the v-PEG-Br was homopolymerized by itself in the presence of CuBr/PMDETA complex in toluene. Argon was passed

into the solution for 2 min. The reaction mixture was then immersed in an oil bath at 80°C and stirred with a magnetic bar. Other conditions are as follows: feed ratio was [v-PEG-Br]:[CuBr]:[PMDETA] = 1 : 1 : 3, and reaction times of 1, 2, 3, 5, 8, 12, and 24 h were applied. After polymerization was complete, the catalyst was removed by adsorption filtration through a silica-gel column using chloroform as the mobile phase, and the resulting polymer was washed with diethyl ether.

Atom transfer radical copolymerization of NIPAM with MIM-ATRPs

The same polymerization condition mentioned above was applied to the copolymerization of NIPAM. In this case, the polymerization medium contained a given amount of NIPAM. The sealed tube was immersed in a preheated oil bath at a desired temperature. The tube was then removed from the oil bath and reaction mixture was dissolved in chloroform, filtered, and dried under vacuum to a constant weight; conversion was then determined gravimetrically. The dried polymer or copolymer was redissolved in chloroform and passed through a silica-gel column to remove the remaining copper catalyst. The sample was then dried again under vacuum up to a constant weight and used in determination of molecular structure with FTIR, ^{1}H NMR, and intrinsic viscosity.

Cloud point measurements

Cloud point measurements were carried out by immersing tubes containing the aqueous PEG-g-PNIPAM graft copolymer solutions in distilled water ranging in temperature from 4 to 65°C.[51] Before measurement of transmittance (%T), the graft copolymer solutions were soaked in distilled water for at least 24 h at each particular temperature. The cloud point was set at the temperature at which the first opaqueness appeared in the solution. The phase transition was also monitored by optical transmittance at 500 nm through a 1-cm sample cell referenced against distilled water, using a Unicam UV2-100 spectrophotometer.

The extent of swelling was characterized by the equilibrium volume swelling ratio (q_v) in water. q_v was calculated by using the equation given in the cited Ref. 52:

$$q_v = 1 + \frac{(q_w - 1)\rho_p}{\rho_s}, \quad (1)$$

where q_w is the ratio of the weights of the gel in the swollen state and the dry state and q_p and q_s are the densities of the polymer and solvent, respectively.

Instrumentation

Viscosity measurements for aqueous solutions of the polymers obtained were done with a Ubbelohde viscosimeter at 25°C.[53]

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. FT-IR and FTIR-ATR (Attenuated Total Reflectance Spectroscopy) spectra were recorded with a Nicolet 520 model FT-IR Fourier Transform Infrared Spectrometer and Perkin Elmer FT-IR Spectrometer 100. UV–vis spectra were recorded on a UNicam UV2-100 spectrophotometer. Thermal analysis of the product was carried out with a Setaram Differential Scanning Calorimetry (DSC) DSC-141 series thermal analysis system under nitrogen. Generally, a dried sample was heated at a rate of 10°C min^{-1} from −50 to 150°C under N_2 atmosphere. The thermal behavior of the samples was investigated with a Du Pont 951 thermogravimetric analyzer.

A CHNS-932 Model LECO Elemental Analyzer was used for the elemental analysis of C, H, and N in products. Molar fractions (mol %) of comonomer units in PEG-g-PNIPAM copolymers were calculated using elemental analysis data (content of N). Elemental analysis of nitrogen in PNIPAM blocks gave the NIPAM amount in the graft copolymer using the following equation:

$$\text{NIPAM (mol \%)} = (N/\text{No}) \times 100, \quad (2)$$

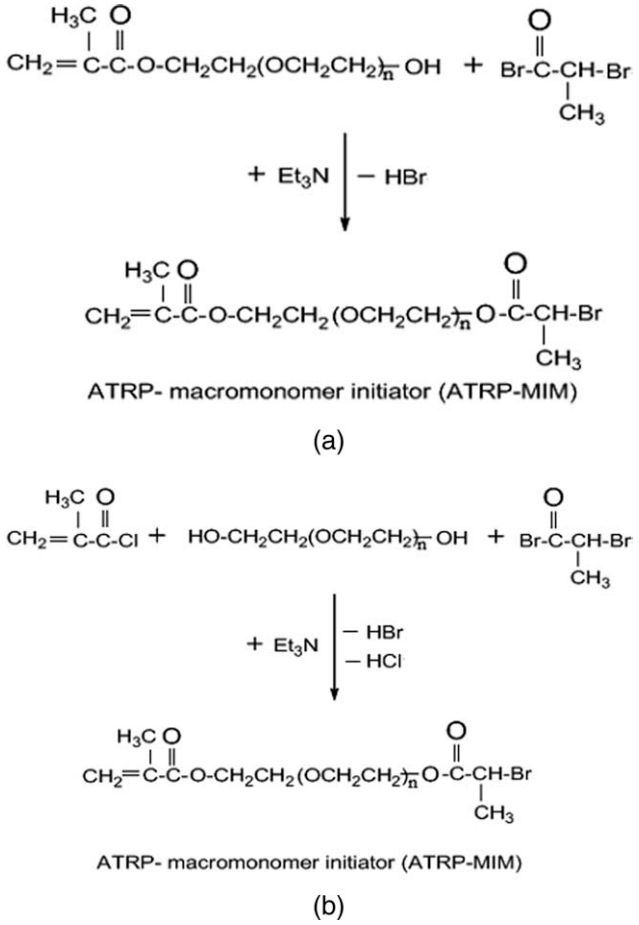
where N is the wt % of nitrogen in the graft copolymer as determined by elemental analysis, and N_o is the wt % of nitrogen content of pure PNIPAM.

Transmission electron microscopy (TEM) experiments were performed on a JEOL 2100 HRTEM microscope, operating at an accelerating voltage of 200 kV. TEM samples were prepared by applying a drop of polymer solution directly onto a carbon-coated copper TEM grid and allowing the solution to evaporate under ambient conditions. After about 3 min, the excess solution was wicked away with a piece of filter paper. The sample was then allowed to dry under ambient conditions. TEM imaging showed micelle structures.

RESULTS AND DISCUSSION

Synthesis of macromer initiators

A series of MIM-ATRPs based on PEG with bromo and methacryloyl ends (*M495, M2203*, and *M4203*, the numbers indicate the theoretical molecular weights) were synthesized according to the basic outline in Scheme 1(a,b). ^{1}H NMR spectra of the v-PEG-OH and v-PEG-Br are shown in Figure 1, which indicates the characteristic signals: δ (ppm),

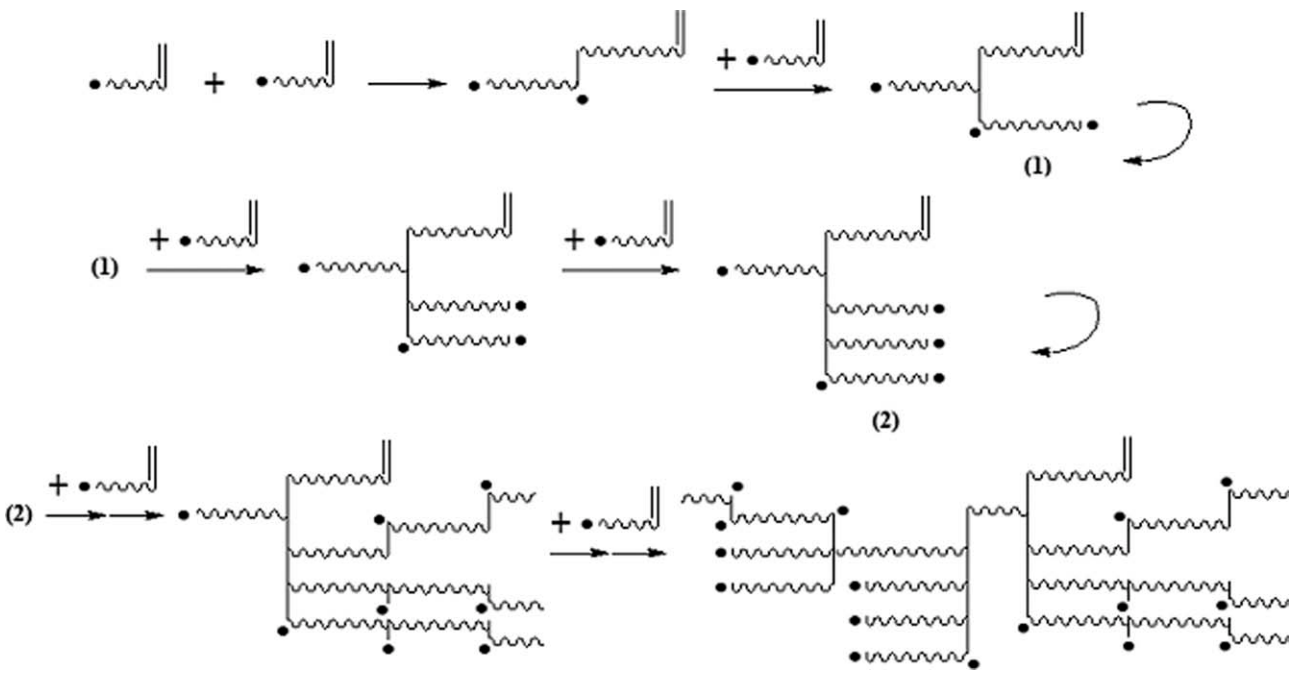


Scheme 1 a. Reaction design of the ATRP-macromonomer initiators (M495). b. Reaction design of the ATRP-macromonomer initiators (M2203 and M4203).

signals at 5.50 and 6.05 for $CH_2{=}C{-}$ of methacrylate, 4.35 for $-CH_2-Br$, 3.55 for OCH_2CH_2O- for PEG, 1.9 for $-CH_3$ of propanoyl, and 1.8 for $-CH_3$ of methacrylate. The signal at 3.62 ppm of the hydroxyl group of the v-PEG-OH (signal g) completely disappeared after the reaction with 2-bromo propanoyl bromide, and two new signals then appeared at 4.35 ppm for $-CH_2-Br$ and 1.9 ppm for $-CH_3$ of propanoyl.

Self-condensing MIM-ATRP (v-PEG-Br) polymerization

Self-condensing MIM-ATRP polymerization was carried out by adding CuBr/PMDETA in toluene at 80°C, leading to hyper branched poly (PEG-methacrylate). The formation of hyper branched PEG-*co*-methacrylate was shown in Schemes 2 and 3(a). The polymerization process caused two new active sites on the second carbon atom of the double bond and on the bromide end of the PEG formed by the ATRP catalyst, as shown in Scheme 2(a,b); thus branching of the v-PEG-Br was improved. Poly(PEG-methacrylate) samples were very hard and brittle and wholly soluble in water. Hyper branched poly(PEG-methacrylate) obtained in this way still contained unreacted double bond and bromide, making further polymerization possible. Figure 1 shows ^{1}H NMR spectrum of the branched poly(PEG-methacrylate). The results and conditions of the self-condensing v-PEG-Br atom transfer radical polymerization are listed in Table I. Intrinsic viscosities of the aqueous solutions of the poly(PEG-methacrylate)s were measured to



Scheme 2 The formation of highly branched poly(PEG-*co*-methacrylate).

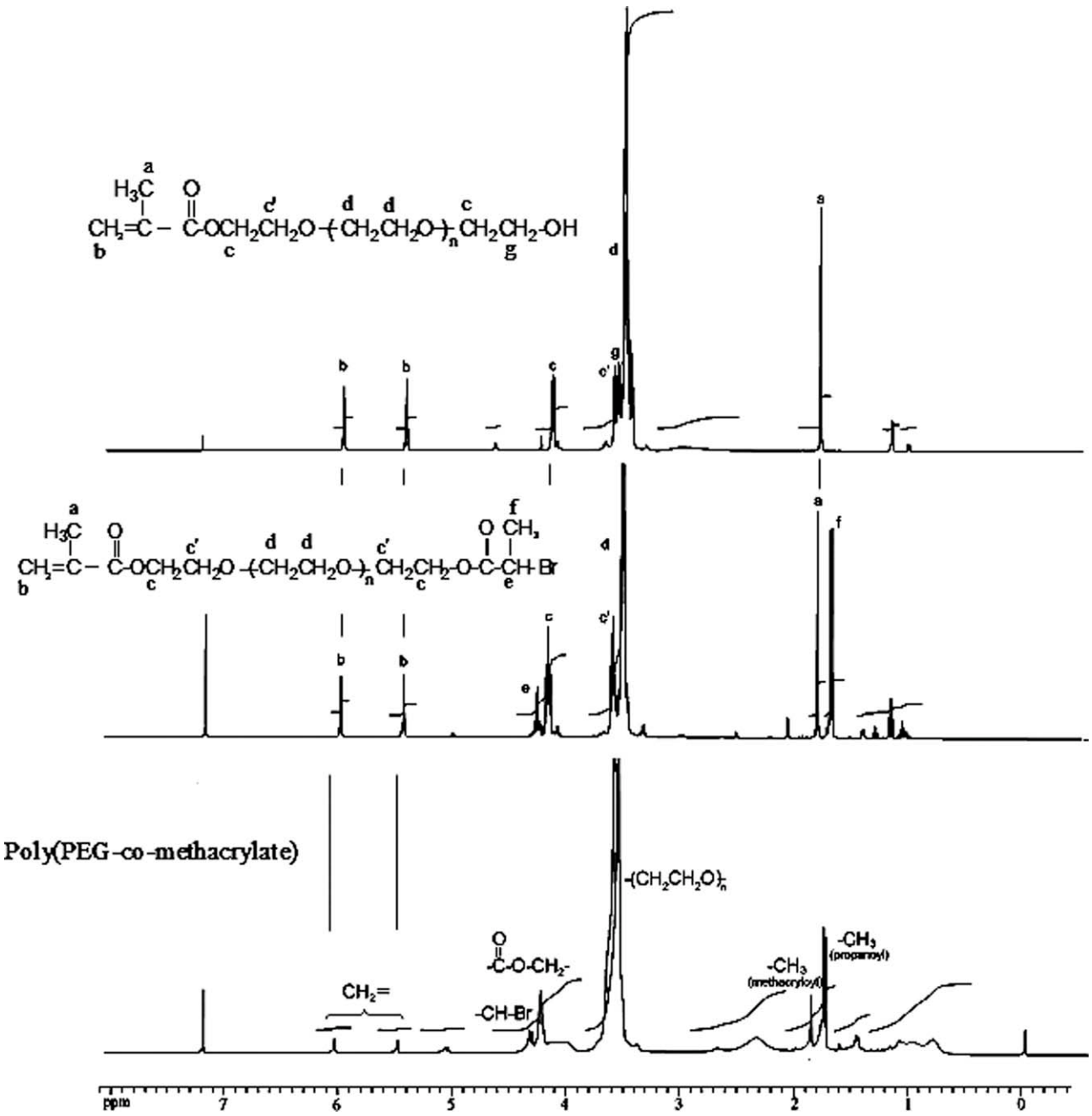
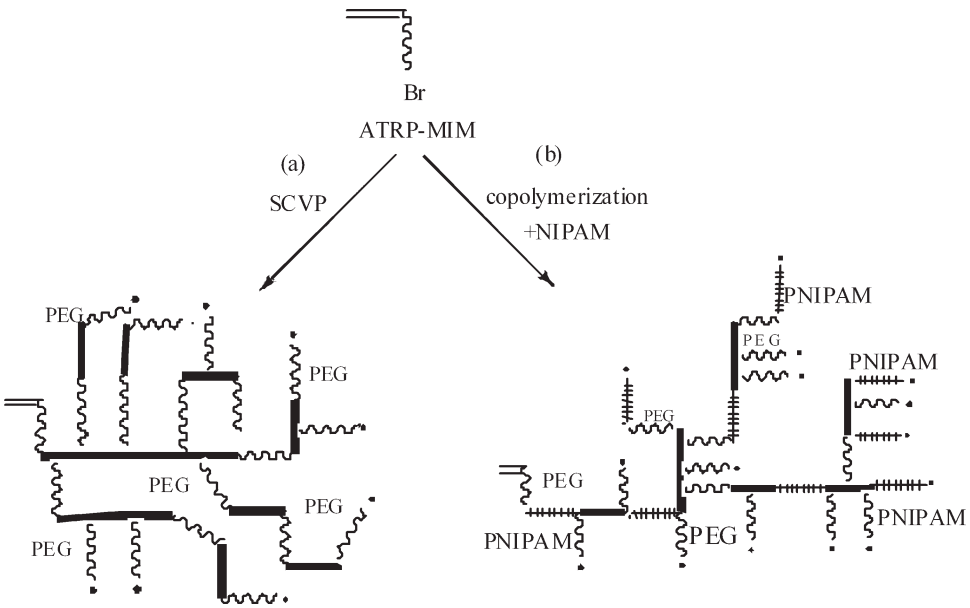


Figure 1 ^{1}H NMR spectra of precursor v-PEG-OH, v-PEG-Br, and Poly(PEG-*co*-methacrylate).

see increases in molecular weights since our GPC columns were not suitable for measuring the molecular weights of these type of polymers. The polymerization time effect on the yield and intrinsic viscosities of the aqueous solution of branched poly(PEG-methacrylate) were studied.

The physical properties of hyperbranched polymers are largely influenced by the extensively branched structures of the molecules.[54] The dissimilarity between hyperbranched and linear polymers is reflected in their intrinsic viscosity behavior.[55,56] Theoretical models have been applied to determine the behavior of hyperbranched polymers both with[57] and without[58] linear polymer units between branch points. The theoretical results indicate that higher intrinsic viscosities can be expected for hyperbranched polymers even with a significant amount of linear polymer units between branch points.

We studied the compactness of the branched polymers to determine the average branching degree. To determine the hydrodynamic dimensions of the hyperbranched polymers in solution, we determined the intrinstic viscosity [η] of the hyperbranched homopolymers. The observed values are collected in Table I.



Scheme 3 (a) Self condensation polymerization (SCVP) of the ATRP-MIM; (b) copolymerization of NIPAM by ATRP-MIM.

The dependence of the dimension of a branched PEG can be expressed by means of the dimensionless parameter[59]

$$g' = [\eta]/[\eta]_L,$$

where $[\eta]_L$ is the intrinsic viscosity of the linear PEG. The values of $[\eta]$ and g' are also listed in Table I. $[\eta]$ of each hyperbranced PEG is higher than that of linear PEG having the same molecular weight. It becomes clear from the g' data that the density of the hyperbranched PEG increases with molecular

TABLE I
Atom Transfer Radical Homo-/Co-Polymerization Behavior of the ATRP-Macromonomer Initiators

	MIM-ATRP									
No	M495 (mmol)	M2203 (mmol)	M4203 (mmol)	Time (h)	Total yield (g)	Total yield (%)	Gel (%)	q_v in H_2O	$[\eta]^a \times 10^{-2}$	g'^b
M495	4.04	–	–	0	–	–	–	–	4.69	1.00
H-1	4.04	–	–	1	1.70	85	4	3.5	4.89	1.04
H-2	4.04	–	–	3	1.77	88	6	2.9	5.12	1.09
H-3	4.04	–	–	5	1.80	90	9	1.5	5.40	1.15
H-4	4.04	–	–	8	1.86	93	12	0.9	5.53	1.18
H-5	4.04	–	–	12	1.89	94	22	0.6	5.71	1.22
H-6	4.04	–	–	24	1.93	96	25	0.4	5.91	1.26
M2203	–	0.91	–	0	–	–	–	–	11.6	1.00
H-7	–	0.91	–	1	0.92	46	–	–	12.25	1.06
H-8	–	0.91	–	3	0.97	48	–	–	13.52	1.17
H-9	–	0.91	–	5	1.22	61	–	–	14.91	1.29
H-10	–	0.91	–	8	1.53	76	–	–	16.44	1.42
H-11	–	0.91	–	12	1.78	89	–	–	18.22	1.57
H-12	–	0.91	–	24	1.81	90	–	–	19.83	1.71
M4203	–	–	0.48	0	–	–	–	–	15.49	1.00
H-13	–	–	0.48	1	0.95	48	–	–	15.16	0.98
H-14	–	–	0.48	3	0.99	50	–	–	18.67	1.21
H-15	–	–	0.48	5	1.24	62	–	–	22.23	1.44
H-16	–	–	0.48	8	1.36	68	–	–	25.75	1.66
H-17	–	–	0.48	12	1.63	82	–	–	29.37	1.90
H-18	–	–	0.48	24	1.78	89	–	–	32.28	2.08

The molar ratio $[I_o]/[CuBr]/[PMDETA]$: 1 /1/ 3 was used.
[a] Measured in chloroform at 25°C.
[b] Branching factor $g' = [\eta]/[\eta]_L$.

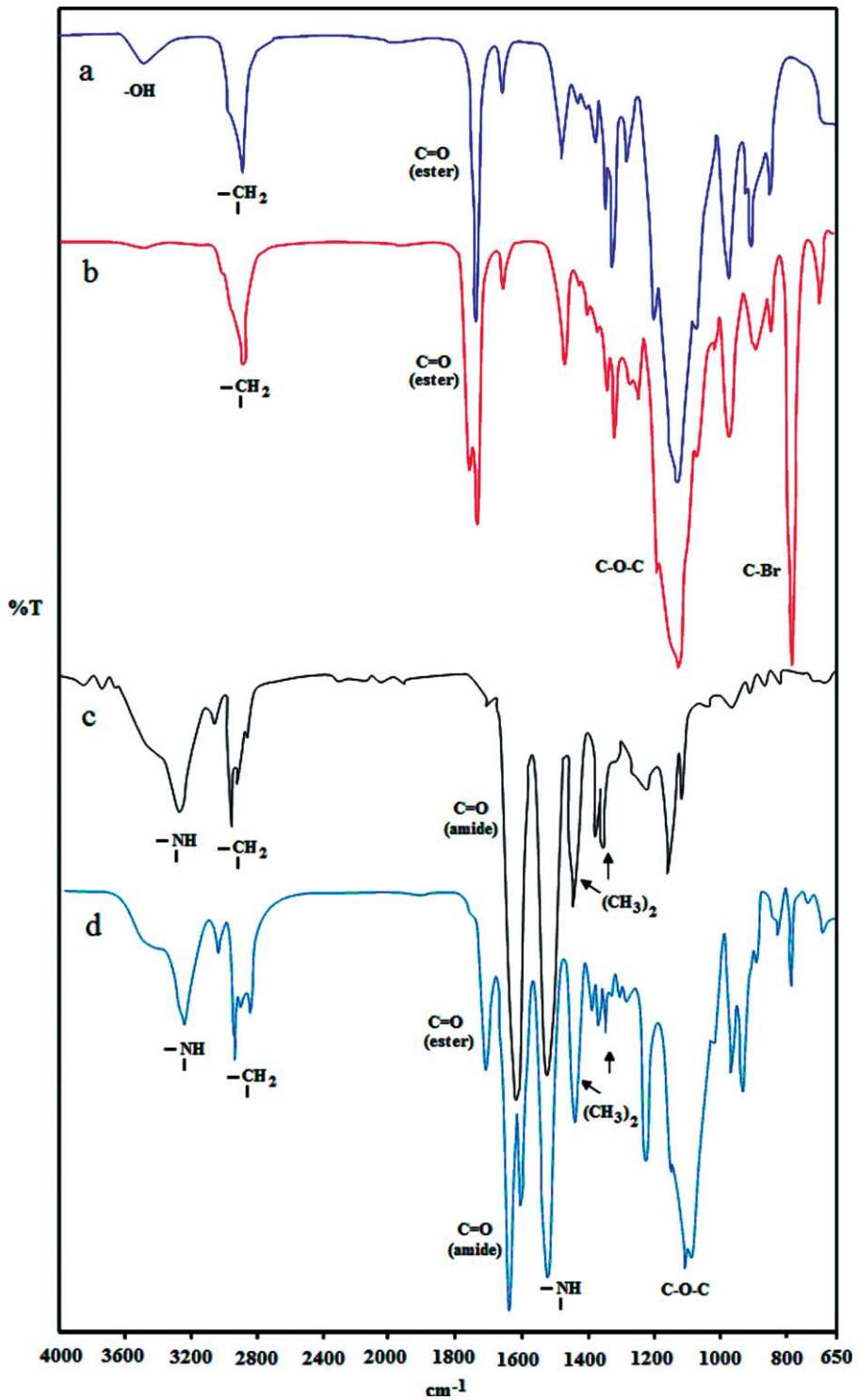


Figure 2 FT-IR spectrum of (a) v-PEG-OH, (b) v-PEG-Br, (c) PNIPAM, and (d) PEG2203-*g*-PNIPAM graft copolymer (N-7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight. The relatively high values of [η] for the produced polymers are indicative of higher hydrodynamic volumes, and are representative of the highly branched nature of these polymers.

In Figure 4, total yield increased as polymerization time increased. The poly(PEG-360-methacrylate) obtained which was contained mostly soluble fraction, with cross-linked polymer varying from 4 to 25 wt % depending on polymerization time in solution. Poly(PEG-2000-methacrylate) and poly(PEG-4000-methacrylate) contained wholly soluble fraction with high polymer yield, ranging from 46 to 90 wt %. The molecular weight of the produced polymer steadily increased with increasing total polymer

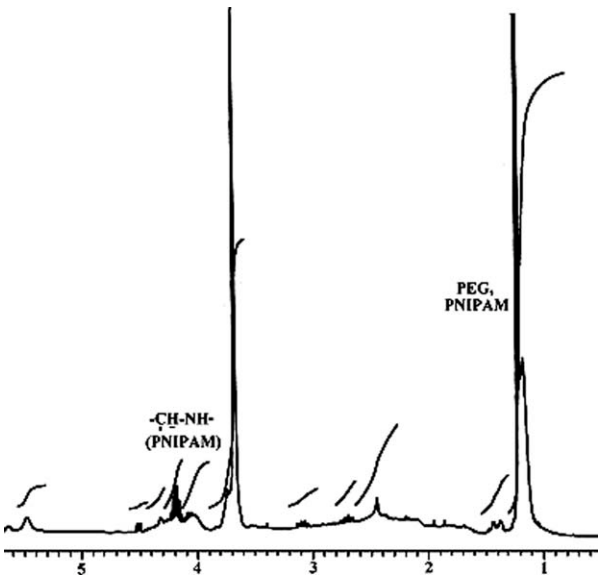


Figure 3 ^{1}H NMR spectrum of PEG-*g*-PNIPAM graft copolymer sample (Run no: N-2).

yield. The increase in M_v with polymerization time is plotted in Figure 5. Homo polymerization of v-PEG-Br macroinimers resulted in PEG-methacrylate polymers via ATRP, contrary to the results obtained from macromonomeric azoinitiators in conventional free radical polymerization leading to higher cross-linked PEG-methacrylates.[8] In this situation, ATRP was found to be a more controllable polymerization method than conventional free radical polymerization in view of fewer cross-linked polymers as well as highly branched polymer production from macromonomer initiators.

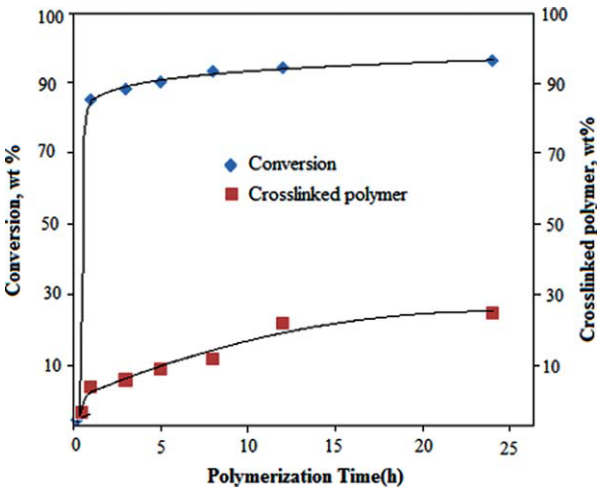


Figure 4 Atom transfer radical homo-polymerization v-PEG-Br-360 in solution at 80°C (solvent toluene): the effect of the polymerization time on the conversion and cross-linked polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis of thermo-responsive graft copolymers

v-PEG-Br macro initiators initiated the copolymerization of NIPAM in the presence of CuBr/PMDETA in toluene at 80°C to obtain hyper branched PEG-g-PNIPAM graft copolymers in high yield. After they were stirred and heated for several minutes, the reaction mixtures turned homogenous. Copolymerization conditions and copolymer analysis are listed in Table II. Scheme 3(b) shows copolymerization of NIPAM by ATRP-MIM. These macro initiators were successfully used to initiate atom transfer radical polymerization of NIPAM. Because of the high reactivity of acrylate monomers, copolymerization of the NIPAM with v-PEG-Br gave a high polymer yield, ranging from 58 to 89 wt %. Table II shows variation in conversion of NIPAM with v-PEG-Br. Increase in the initial feeding of NIPAM caused an increase in the molecular weight of graft copolymers.

Elemental analysis of nitrogen was also useful in determining the N-content of graft copolymers. The N-content of a copolymer rises with an increase in the initial feed ratio of NIPAM. The varying polymer yield and its PEG content in relation to the initial feed ratio of NIPAM are presented in Table II. These graft copolymers contained PNIPAM blocks between 5.5 and 80 wt %, depending on the initial feed ratio.

The FTIR spectra of the graft copolymers were taken as KBr samples. The signal carbonyls of amide groups at 1660 cm^{-1} and —NH— groups at 3320 cm^{-1} attributed to the PNIPAM sequence were also accompanied by the presence of a 2950 cm^{-1} absorption band, characteristic of the PEG segment. The signal carbonyls of ester groups at 1740 cm^{-1} and ether groups at 1160 cm^{-1} are attributed to the PEG. Figure 2 shows a typical FTIR spectrum of v-PEG-OH, v-PEG-Br, PNIPAM, and PEG-g-PNIPAM graft

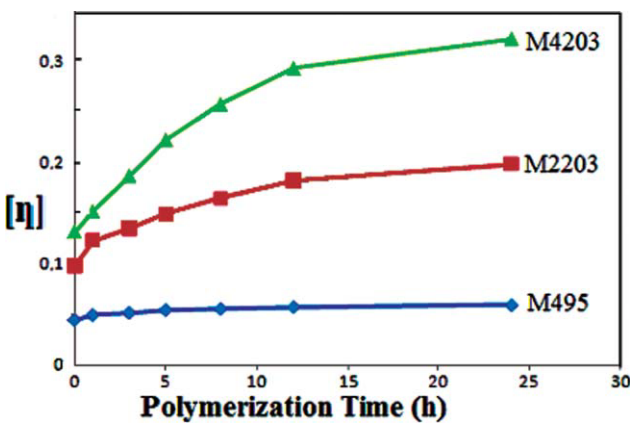


Figure 5 Atom transfer radical homo-polymerization of MIM-ATRP at 80°C: the effect of the polymerization time on the [η] of the poly(PEG-co-methacrylate)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Results and Conditions of the Atom Transfer Radical Polymerization of NIPAM with MIM-ATRP at 80°C

No	MIM-ATRP M495 (mmol)	MIM-ATRP M2203 (mmol)	MIM-ATRP M4203 (mmol)	NIPAM (mmol)	Polym yield (g)	Polym yield (wt %)	NIPAM (%)[a]	$[\eta] \times 10^{-2}$
N-1	4.04	–		12.1	2.70	80	49	4.87
N-2	4.04	–		20.3	3.70	86	55	5.22
N-3	4.04	–		40.4	5.83	89	80	6.32
N-4	–	0.91	–	4.5	1.47	58	25	12.35
N-5	–	0.91	–	9.0	2.04	67	31	15.41
N-6	–	0.91	–	18.1	2.84	70	55	18.25
N-7	–	0.91	–	45.4	5.34	74	63	23.24
N-8	–	–	0.48	2.4	1.42	62	5.5	25.15
N-9	–	–	0.48	4.7	1.62	64	27	27.36
N-10	–	–	0.48	9.5	2.07	67	39	29.15
N-11	–	–	0.48	23.8	3.22	69	47	32.86
N-12	–	–	0.48	35.7	4.60	76	67	36.12

The molar ratio, $[I_o]/[CuBr]/[PMDETA]$: 1 / 1 / 3 was used.
[a] Calculated from elemental analysis.

copolymer (Run no: N-2) with the characteristic bands of related segments.

^{1}H NMR spectra of the graft copolymer samples of PEG-g-PNIPAM contained characteristic peaks: δ (ppm), signals at 3.55 for OCH_2CH_2O— for PEG, 1.9 for —CH_3 of propanoyl, and 1.8 for —CH_3 of methacrylate. In addition, the signals of protons in the PNIPAM graft appear in the spectrum at 1.1–1.4 ppm (—CH_3), 2.0–2.2 ppm (—CH_2—), and 3.8–4.1 ppm (—CH—). Figure 3 shows a typical ^{1}H NMR spectrum of a PEG-g-PNIPAM graft copolymer (Run no: N-3) with the characteristic bands of related segments.

A thermal analysis of graft copolymers was performed by DSC and TGA (Table III). Glass transition temperatures, T_g, and melting temperatures, T_m, for each sample were observed to be considerably lower than those of the PNIPAM homopolymer (T_g = 135 °C,[60]). A plasticizer effect of PEG in graft copolymers was observed, indicating a lower glass transition and melting than that of pure PNIPAM.

T_ms were observed for the MIM-ATRP samples for vPEG-Br-360 (T_m = 50 °C), vPEG-Br-2000 (T_m = 54 °C) and vPEG-Br-4000 (T_m = 59 °C). T_ms and T_gs were observed for the poly(PEG-*co*-methacrylate) samples for H-5 (T_g = −10°C), H-12 (T_m = 51°C), and H-17 (T_m = 57°C). T_ms were observed for the PEG-g-PNIPAM graft copolymer samples for N-1 (T_g = −20°C), N-2 (T_g = −20°C), N-3 (T_m = 55°C), N-4 (T_m = 45°C), N-5 (T_m = 42°C), N-6 (T_m = 37°C), N-7 (T_m = 43°C), N-8 (T_m = 53°C), N-9 (T_m = 42°C), N-10 (T_m = 47°C), and N-12 (T_m = 46°C) (Fig. 6). Furthermore, a plasticizer effect of PEG was clearly observed upon insertion of the PEG blocks into the PNIPAM graft copolymers.

Decomposition temperatures, T_d, of the graft copolymers were similar to that of PNIPAM at around 431°C.[60] The plasticizing effect of PEG blocks reduced the decomposition temperatures of PNIPAM conjugates 10–20°C (see Table III, Fig. 7). The same behavior was observed in our previous research.[61,62]

TABLE III
Thermal Properties of the PEG-*g*-PNIPAM Graft Copolymers and their Precursors

Sample	DSC (°C) T_g	DSC (°C) T_m	TGA (°C) T_{d1}	TGA (°C) T_{d2}	TGA (°C) T_{d3}	TGA (°C) T_{d4}
PNIPAM [Ref. 60]	135	–	–	–	–	431
v-PEG-Br-360	–	50	60	300	330	390
v-PEG-Br-2000	–	54	–	180	–	395
v-PEG-Br-4000	–	59	–	–	–	400
H-5	−10	–	–	300	–	405
H-12	–	51	–	–	–	410
H-17	–	57	–	–	–	410
N-1	−20	-	–	140	260	405
N-2	−20	-	–	140	265	410
N-3	–	55	–	140	–	400
N-4	–	45	–	140	–	410
N-5	–	42	–	155	–	405
N-6	–	37	–	160	–	410
N-7	–	43	–	155	–	415
N-8	–	53	–	140	–	400
N-9	–	42	–	135	–	400
N-10	–	47	–	145	–	400
N-12	–	46	–	150	–	410

TABLE IV
LCST Values of the Selected Hyper Branched PEG-*g*-PNIPAM Copolymers: N-3, N-7, N-11, N-12 in Table II

Sample	LCST (°C)
N-3	36
N-7	33
N-11	36
N-12	33

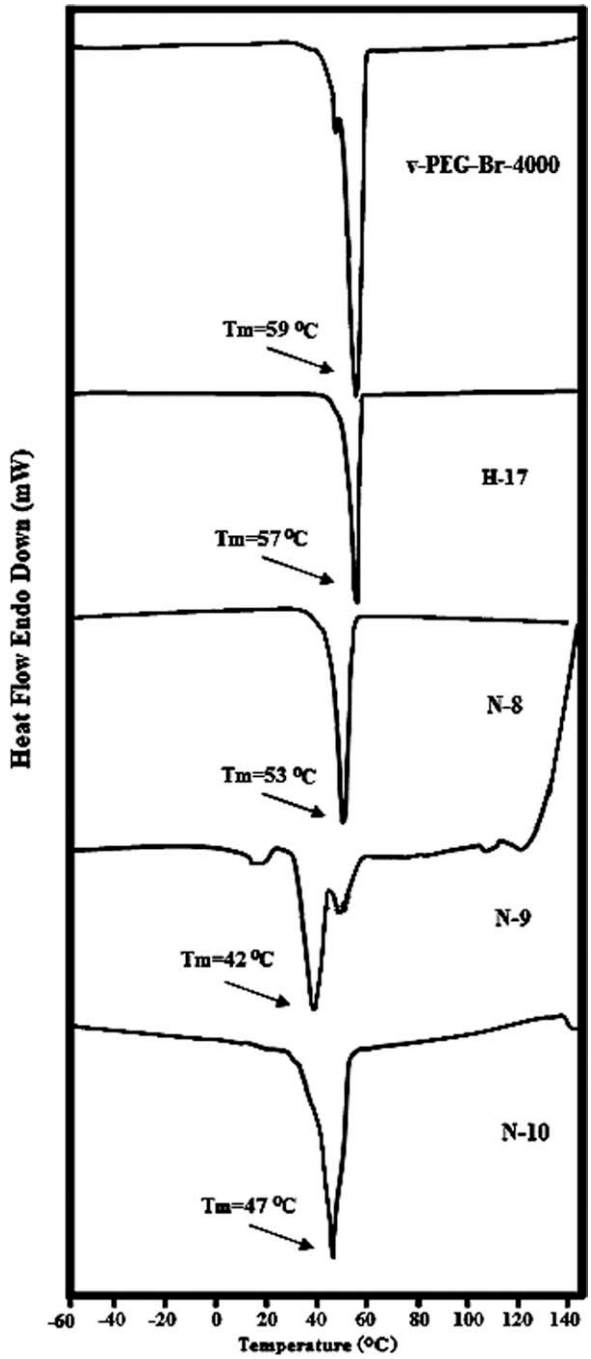


Figure 6 DSC thermogram of the v-PEG-Br-4000, Poly(-PEG-*co*-methacrylate) (Sample: H-17, in Table III) and PEG4203-*g*-PNIPAM graft copolymers (Samples: N-8, N-9, N-10, in Table III).

Cloud point measurements

Typical optical density curves are shown in Figure 8 for 10 wt % graft copolymer solutions as a function of heating rate. The reduction of UV transmittance observed upon heating was a rather abrupt phenomenon, while the accompanying 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 4–65°C. The temperature dependence of the transmittance of PNIPAM graft copolymers is shown in Figure 8. From the plots of %*T* versus temperature, we found the LCSTs of the copolymers to be 33°C for N-7 and N-12, and 36°C for N-3 and N-11, respectively, corresponding to the increasing content

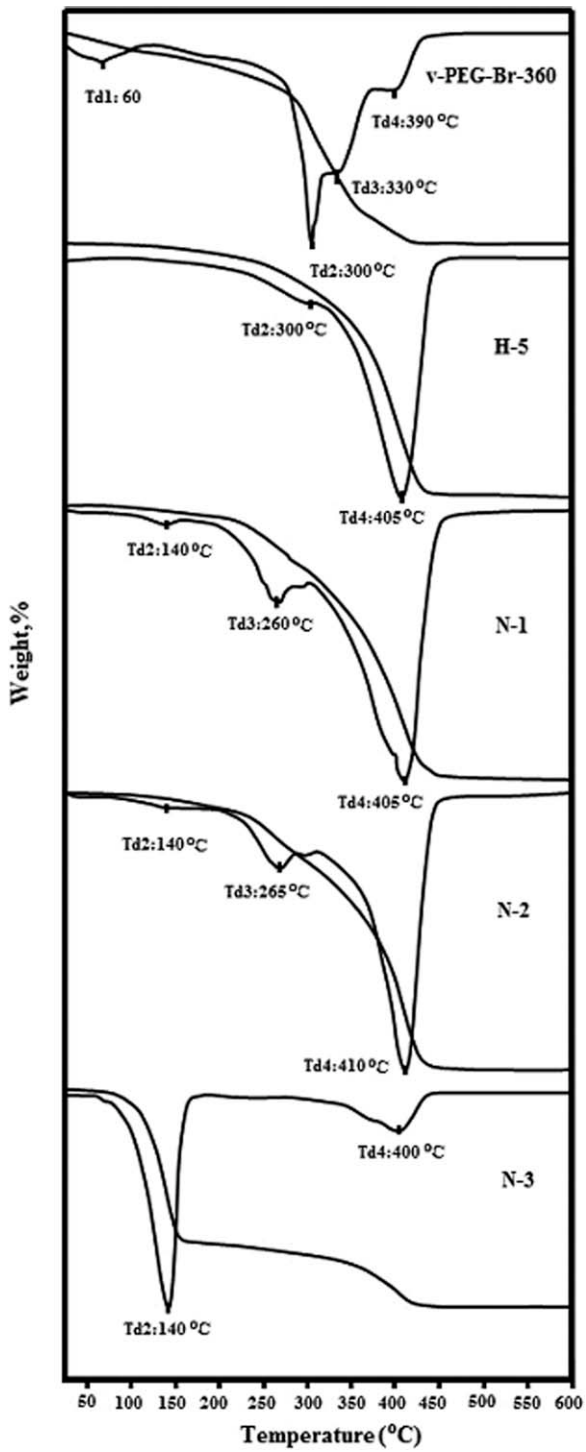


Figure 7 TGA thermogram of the v-PEG-Br-360, Poly(-PEG-*co*-methacrylate) (Sample: H-5, in Table III) and PEG495-*g*-PNIPAM graft copolymers (Samples: N-1, N-2, N-3, in Table III).

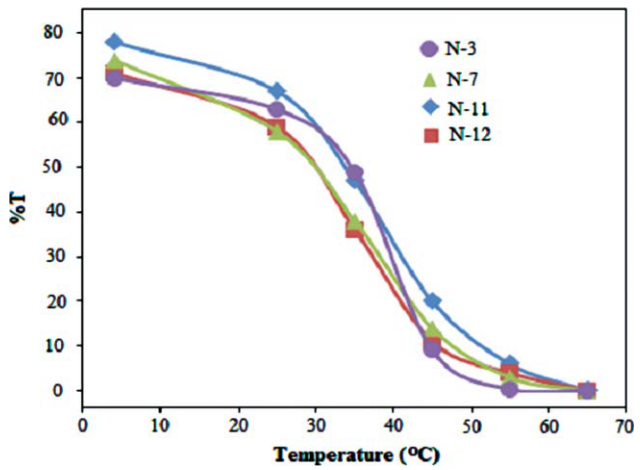


Figure 8 Temperature dependence of equilibrated swelling ratio of PNIPAM graft copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of hydrophilic units (PEG).[51] Enhanced hydrophilicity of the copolymers causes higher LCST values than the LCST value of PNIPAM homo polymer, 32°C. Block 1 was also found to retain a thermo-responsive phase-transition property based on the results for turbidity change in aqueous solution with increasing concentration and time at 35°C. It has been reported that increased molecular weight of the PEG segment in PEG-based block copolymers leads to a decrease in LCST.[39,40]

Micelle formation and surface morphology of the graft copolymer

Micellization occurs when the block copolymer is dissolved in a large amount of a selective solvent for one of the blocks.[63,64] Under these circumstances, the polymer chains tend to organize themselves into a variety of structures, from micelles or vesicles to cylinders. The soluble block is oriented toward the continuous solvent medium and becomes the "corona" of the micelle formed, whereas the insoluble part is shielded from the solvent in the "core" of the structure (Fig. 9).

Amphiphilic block copolymers can form various vesicular architectures in solution. The vesicle formation is of fundamental and practical importance, because it has many potential applications in areas such as microreactors, microcapsules, and drug delivery systems.[65–71] To investigate micelle formation of an amphiphilic copolymer, we took TEM images of the samples (N-7 and N-12) in water solutions at 60°C, as shown in Figures 9(a,b), respectively, in which we observed spherical micelles after micelle solutions were evaporated on a TEM grid. This result suggests that the amphiphilic copolymer micelles have water-insoluble PNIPAM cores and water-soluble PEG coronas at 60°C. Samples for TEM were prepared below and above the LCST (from solutions of 5 mg mL^{-1} of hyper branched polymer P5, Fig. 9). Above the LCST, the images show well-dispersed and well-defined aggregates (with regular shapes and sizes) formed from hyper branched polymers, while below the LCST, no self-assembled nanoparticles were observed by TEM, in agreement with the cited Ref. 72.

CONCLUSIONS

A novel macromonomer initiator for ATRP was synthesized from the commercial methacryloyl polyethylene glycol and 2-bromo propanoyl bromide.

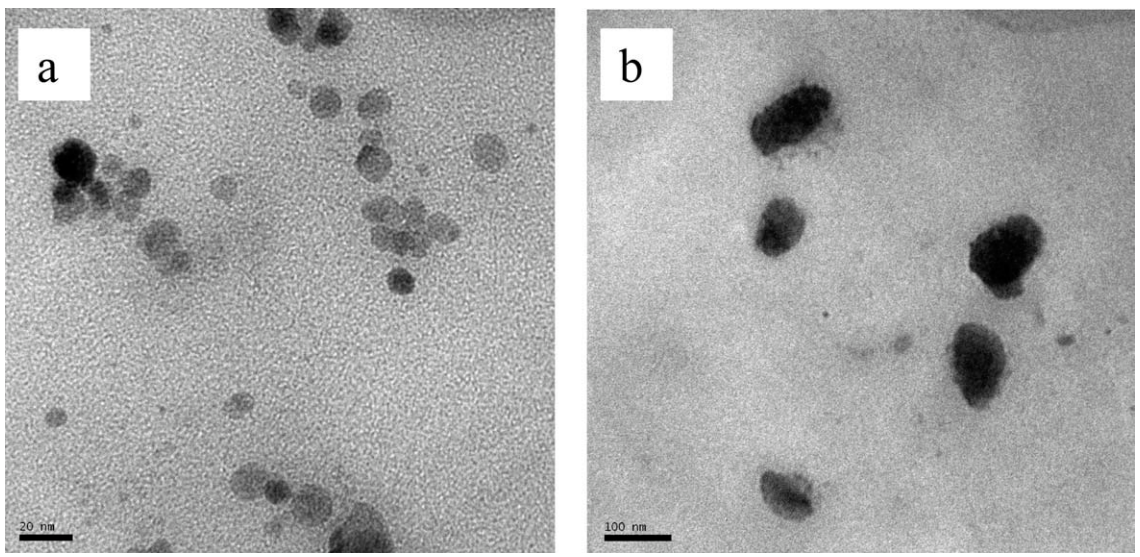


Figure 9 TEM images of the PEG-g-PNIPAM graft copolymer micelles (a) PEG2203-*g*-PNIPAM (N-7) (bar: 20 nm) and (b) PEG4203-*g*-PNIPAM (N-12) at 60°C (bar 100 nm).

Self-condensing atom transfer radical polymerization using the CuBr/ligand catalyst system at 80°C gave branched poly(PEG-methacrylate) with low cross-linked polymer fraction (4–25 wt %), contrary to the macromonomer azo initiators for conventional free radical polymerization. It is also concluded that ATRP of macromonomer initiators is a more controllable polymerization method than conventional free radical polymerization in view of fewer cross-linked polymers and highly branched polymer production. PNIPAM-*g*-PEG graft copolymers obtained by macroinimers can have higher porosity in their branching structure than classical cross-linked polymers obtained by macro cross-linkers. These responsive polymers show improved sensitivity of swelling behaviors and have potential field applications in a new application sector of industry and bioengineering.

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