Hydrogels by Atom Transfer Radical Polymerization. I. Poly(*N*-Vinylpyrrolidinone-*g*-Styrene) via the Macromonomer Method

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ABSTRACT: Atom transfer radical polymerization has been used to prepare well-defined vinyl macromonomers of polystyrene using vinyl chloroacetate as an initiator. Because styrene and vinyl chloroacetate do not copolymerize, no branching or incorporation of the initiator into the backbone was observed. Macromonomers of several molecular weights were prepared and copolymerized free radically with *N*-vinylpyrrolidinone in varying feed ratios in order to produce poly(NVP-*g*-Sty) graft copolymers. The macromonomers used were of sufficiently high molecular weight to form physical crosslinks in solvents which favor the hydrophilic NVP, such as water, which prevent the copolymer from dissolving and cause it to swell. These materials, therefore, formed hydrogels of swellabilities in water exceeding 95%, depending on the amount of styrene that was incorporated into the copolymer. Limitations of and alternatives to this method are also discussed. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 36: 823–830, 1998
Keywords: atom transfer radical polymerization; poly(*N*-vinylpyrrolidinone-*g*-styrene; macromonomer method

INTRODUCTION

Recently, new methods of controlling radical polymerizations[1] have resulted in the ability to form many new materials and molecular architectures that were not possible to obtain using other known methods of controlled polymerization.[2] Atom transfer radical polymerization (ATRP) is one such method of "living" radical polymerization that uses a catalytic amount of a copper/dipyridyl complex.[3] By deactivating the radical chain ends reversibly, termination reactions are significantly reduced, resulting in degrees of polymerization close to theoretical values based on the ratio of concentrations of reacted monomer to initiator and narrow molecular weight distributions. One approach to expanding the application of these new processes is to use them in combination with other methods to improve their efficiency or versatility.

An example of this approach is the preparation of graft copolymers. Graft copolymers are generally made using one of three methods: grafting-onto, grafting-from and grafting-through. Conventionally, grafting-through involves the copolymerization of macromonomers, made from either other living methods or conventional radical methods,[4,5] with other small monomers. Because radical polymerization can be applied to a wider variety of monomers than other "living" methods, controlled radical polymerization would provide an excellent means of expanding the versatility of the macromonomer method, particularly by increasing the number of monomers available for making macromonomers and the ease with which they can be made.

In addition to increasing the versatility of the

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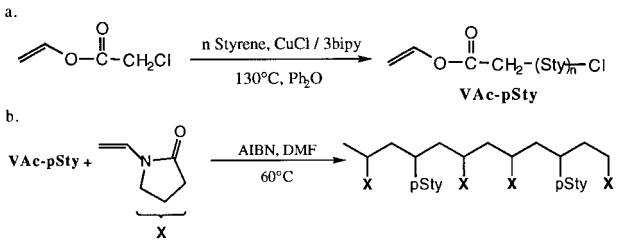

Scheme 1. (a) Preparation of the VAc-pSty macromonomer via ATRP. (b) free radical copolymerization of VAc-pSty with NVP.

macromonomer method, there is the possibility of facilitating the preparation of specific, novel materials using this method. For example, hydrogels, materials that swell but do not dissolve in water, have been traditionally made using chemically crosslinked water-soluble polymers or block or graft copolymers containing hydrophobic and hydrophilic segments. The block and graft copolymers have been shown to exhibit greater mechanical strength than crosslinked materials. For example, poly(2-hydroxyethyl methacrylate-*g*-styrene) has been shown to display greater mechanical strength than crosslinked poly(2-hydroxyethyl methacrylate) homopolymers.[6] In addition, like other thermoplastics, hydrogels that utilize hydrophobic microdomains can also be homogenized and molded after phase separation (physical crosslinking) into any desired shape.[7]

Water-swellable graft copolymers typically possess a hydrophilic backbone and hydrophobic side chains, as opposed to the reverse structure, to prevent micellization. The degree to which a given hydrogel swells in or absorbs water is determined by both the size and number of the side chains in the molecules.[8] There is a low molecular weight limit below which there is no microphase separation in the copolymer[9] and no physical crosslinking of the side chains to prevent dissolution. This limit is significant to the synthesis of the copolymers as well, because it has a dramatic effect on the reactivity of macromonomers, which is discussed later.

The following is an example of the use of ATRP in making amphiphilic graft copolymers that swell in water. Polystyrene macromonomers were made in a controlled fashion using ATRP and were subsequently used in the preparation of graft copolymers via free radical copolymerization with *N*-vinylpyrrolidinone (NVP).

EXPERIMENTAL

Materials

Copper(I) chloride was stirred in acetic acid to remove copper(II) and then washed with ethanol and dried in a vacuum oven. 2,2′-Bipyridyl (bipy) was recrystallized from ethanol. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. All monomers (styrene, vinyl chloroacetate and NVP) were deinhibited by passing through an alumina column. Diphenyl ether, DMF, benzene and heptane were used as received from Aldrich Chemicals. All solvents and monomers were degassed with bubbling argon for a minimum of 30 min prior to use.

Polystyrene with Vinyl Acetate End Group (VAc-pSty), ($M_{n,\mathrm{th}}$ = 5,000)

Cu(I)Cl (0.5188 g) and bipy (2.40 g) were added to a 100-mL round-bottom flask and sealed with a rubber septum. The contents of the flask were degassed by applying a vacuum and backfilling with argon three times. Previously degassed styrene (30.0 mL) and diphenyl ether (30.0 mL) were then added to the flask via syringe and the contents became deep red in color. Vinyl chloroacetate (VAc-Cl) (0.53 mL) was also added at this time. The solution was stirred at 130°C for 6 h. Conversion was measured using ^{1}H-NMR (85%). The solution was precipitated into methanol (600 mL). The light green solid was redissolved in THF, filtered over alumina to remove the copper salts, and reprecipitated into methanol (600 mL) two more times. The final product was a fluffy white powder. (GPC: M_n = 5800; M_w/M_n = 1.12). The yield was 80%.

VAc-pSty ($M_{n,\mathrm{th}}$ = 10,000)

The procedure was the same as above. Cu(I)Cl = 0.5188 g; bipy = 2.40 g; Sty = 60.0 mL; diphenyl ether = 60.0 mL; VAc-Cl = 0.53 mL; reaction time = 24 h. (GPC: M_n = 11,900; M_w/M_n = 1.15). The yield was 81%.

VAc-pSty ($M_{n,\mathrm{th}}$ = 15,000)

The procedure was also the same as above. Cu(I)Cl = 0.173 g; bipy = 0.8 g; Sty = 30.0 mL; diphenyl ether = 30.0 mL; VAc-Cl = 0.177 mL;

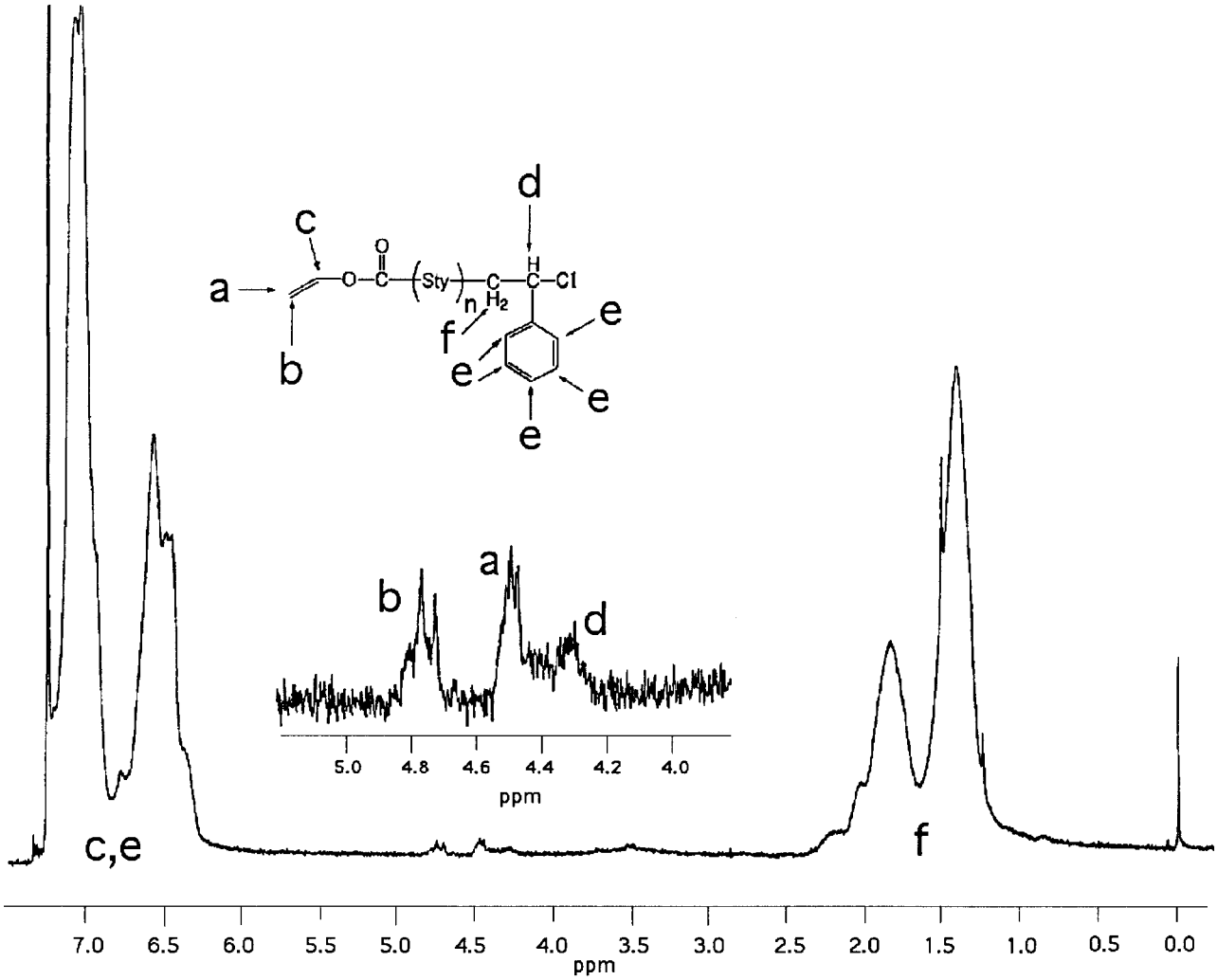

Figure 1. ^{1}H-NMR of VAc-pSty M_n = 5800 (GPC) in *d*-chloroform. M_n (NMR) = 5200.

reaction time = 37 h. (GPC: M_n = 15,900; M_w/M_n = 1.18). The yield was 58%.

General Procedure for Preparation of Poly(*N*-vinylpyrrolidinone-*g*-Styrene):

Copolymerizations of each size macromonomer were carried out with NVP in varying feed ratios from 10 to 50 wt %. The VAc-pSty macromonomer and AIBN (0.14 mol % relative to NVP) were added to a 25-mL round-bottom flask and sealed with a rubber septum. The flask was then degassed by applying a vacuum followed by an argon back-fill three to five times. The appropriate amounts of degassed NVP and DMF (50 vol % relative to the total amount of both monomers) were added by syringe. The reaction was stirred at 60°C for the desired time. The reaction mixtures were relatively viscous and required dilution with DMF. The mixture was precipitated into water, filtered over a medium porosity 150-mL fritted glass funnel, and dried in a vacuum oven overnight (90°C).

Residual macromonomer was removed by dissolving in hot benzene and precipitating into boiling heptane four to eight times until GPC showed no remaining macromonomer.

CHARACTERIZATION

A Waters 510 LC Pump connected to a Waters 410 differential refractometer with DMF as the carrier solvent and linear 500 and 1000 Å Pheno-

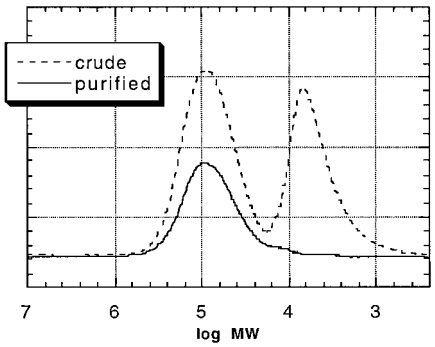

Figure 2. GPC traces of crude and purified product from the copolymerization of NVP with VAc-pSty (M_n = 5800; PDI = 1.12). Purified copolymer M_n = 263,000; PDI = 2.36; wt % sty = 19.2 [wt % (th) = 30]; average number of grafts per chain = 8.7. Product was purified after four precipitations from hot benzene into boiling heptane.

gel columns were used for gel permeation chromatography (GPC). Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Bruker Spectrometer. Differential scanning calorimetry (DSC) was performed on a Rheometric Scientific DSC Plus using a scanning rate of 5°C/min. Thermal gravimetric analysis (TGA) was performed on a Rheometric Scientific TGA 1000 with a scanning rate of 10°C/min.

RESULTS AND DISCUSSION

Macromonomers of polystyrene of various lengths were made via ATRP using vinyl chloroacetate as the initiator and CuCl/bipy as the catalyst (Scheme 1a). There was little or no incorporation of vinyl acetate into the polymer backbone due to the extremely low reactivity of styrene radicals for vinyl acetate (r_{sty} = 42; r_{VAc} = −0.04).[10] The presence of the vinyl end group was confirmed by the observation of vinyl protons using ^{1}H-NMR of the purified macromonomer (Fig. 1). Incorpora-

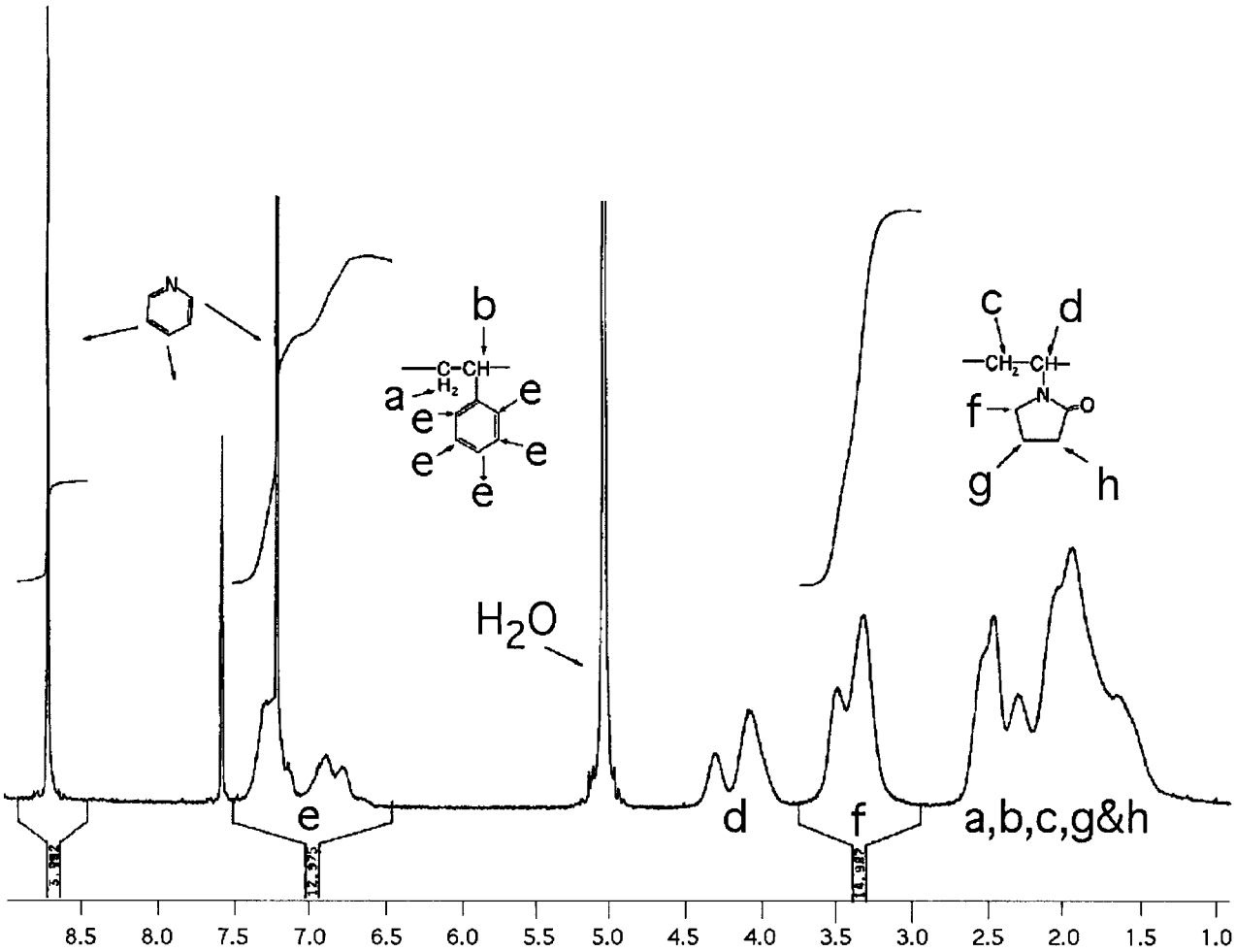

Figure 3. ^{1}H-NMR of poly(NVP-*g*-Sty) in d_5-pyridine.

Table I. Yield and Composition of Copolymers Containing Macromonomer with M_n = 5800

Theoretical wt % Sty	Actual wt % Sty	M_n Copolymer	PDI	% Yield	Avg. Number of Grafts per Chain	% Conv. Sty	% Conv. NVP
50	35.4	95,500	2.80	19.6	5.8	14	25
40	34.2	316,000	5.90	48.9	18.6	42	53
30	19.2	264,000	2.36	15.8	8.7	10	18
20	13.0	219,000	2.45	20.0	4.9	12	21
10	7.73	185,000	1.81	22.1	2.5	16	23

tion of vinyl chloroacetate in the backbone of the smallest macromonomer was also confirmed to be below the limit of detection by comparing molecular weights determined from ^{1}H-NMR as shown in Figure 1 with the molecular weight obtained from GPC. Molecular weight was determined from the NMR by comparing the integrated area of the peak corresponding to the vinyl end group (4.6–4.9 ppm) with that of the aromatic region due to the phenyl groups on styrene (6.0–7.5 ppm). Molecular weights of the products were in good agreement with theoretical values and polydispersities were narrow (<1.2).

Conventional free radical copolymerization was used in the second step (Scheme 1b) to avoid initiation of the halogen terminated ends of the macromonomers, the formation of diblock copolymer side chains, or macromonomers and cross-linking. After the absence of macromonomer was confirmed by the presence of a monomodal distribution in the GPC, indicating that only the copolymer was remaining (Fig. 2), the relative content of macromonomer in the copolymer was determined by ^{1}H-NMR. The wt % of styrene in the copolymer, W_s, was calculated by comparing the area of the aromatic region (A_{ar}, 6.5–7.5 ppm), corrected for solvent (d_5-pyridine; A_p, 8.5–8.9 ppm), vs. the area of the α-protons of the pyrrolidinone ring (A_α, 3.0–3.75 ppm; splitting due to stereoisomers) as shown in Figure 3 and eq. (1):

$$W_s = \frac{\left[\dfrac{(A_{ar} - A_p)}{5} \cdot 104\right]}{\left\{\left[\dfrac{(A_{ar} - A_p)}{5} \cdot 104\right] + \left(\dfrac{A_\alpha}{2} \cdot 111\right)\right\}} \quad (1)$$

Using this number (W_s) and the number average molecular weights of the copolymer ($M_{n\,(\mathrm{co})}$) and macromonomer ($M_{n\,(\mathrm{p(Vac\text{-}Sty)})}$) determined by GPC, the average number of grafts per chain, N_g, was calculated by determining the wt % of the copolymer due to polystyrene and dividing by $M_{n\,(\mathrm{p(Vac\text{-}Sty)})}$ as shown in eq. (2):

$$N_g = \frac{W_s \cdot M_{n\,(\mathrm{co})}}{M_{n\,(\mathrm{p(Vac\text{-}Sty)})}} \quad (2)$$

This is only an estimated value, due to the fact

Table II. Yield and Composition of Copolymers Containing Macromonomer with M_n = 11,900

Theoretical wt % Sty	Actual wt % Sty	M_n Copolymer	PDI	% Yield	Avg. Number of Grafts per Chain	% Conv. Sty	% Conv. NVP
50	39.7	65,700	1.58	42.4	2.2	34	51
40	46.5	28,200	2.0	43.0	1.1	50	39
30	30.4	83,300	1.77	28.3	2.1	29	28
20	23.7	114,200	1.80	24.8	2.3	29	24
10	N/A[a]	N/A[a]	N/A[a]	N/A[a]	N/A[a]	N/A[a]	N/A[a]

[a] Copolymer formed a surfactant in water and was not isolated.

Table III. Swelling Properties of Graft Copolymers with Side Chains of M_n = 5800

wt % Sty ⇒	35.4	34.2	19.2*	13.0	7.73
Q (%)	387	661	538	1228	3311
H (%)	74.1	84.9	81.4	91.9	97.0

[a] Film sample cast from THF due to poor precipitation in water.

that the molecular weights determined by GPC may be different from the real molar masses because they are determined vs. a linear polystyrene standard.

The resulting values for the series of copolymers using the macromonomers with a number-average molecular weight of 5800 and 11,900 are listed in Tables I and II, respectively, along with the corresponding values of total molecular weight, polydispersity, and yield. Conversions were calculated using the mass of polymer obtained, starting quantities of monomer and macromonomer, and the wt % of styrene calculated from NMR. With regards to NVP, this number is defined only as monomer incorporated into copolymer because any homopolymer formed (pNVP) would have been removed during purification. Hence, those particular numbers may be low estimates. Reaction times were well in excess of that necessary to decompose all of the AIBN present, and little or no increase in conversion was observed beyond these points.

In the case of the macromonomer with M_n = 15,900, there was little or no incorporation of macromonomer in any of the copolymerizations, and removal of macromonomer was increasingly difficult due to the poor solubility of higher molecular weight polystyrene in heptane.

An unusual correlation has been observed in the literature[11] between molecular weight of the macromonomer and its reactivity. As mentioned earlier, there is a graft molecular weight limit above which there is a phase separation, observable in the divergence of the glass transition temperature into two points, corresponding to the polymers forming the grafts and backbone. This is a property of principle concern in the formation of hydrogels, because it is also at and above this point where physical crosslinking is promoted and swellability vs. solubility of the copolymer dominates. Whereas the reactivity of the macromonomer decreases as molecular weight increases once this limit is exceeded, reactivity of the macromonomer increases with molecular weight below this limit. The effect at higher molecular weight has been attributed to steric affects in which the random coil structure of the macromonomer and its hydrodynamic volume in solution effectively block the approach of the propagating chain by reducing accessibility of the end groups on the macromonomer and is referred to as the Kinetic or Excluded Free Volume Effect.[12] This is one factor that prevents the ability to prepare well-defined graft-copolymeric architectures using moderate to high molecular weight macromonomers; in this case, with macromonomers of molecular weights at or above at least 10,000 or below where the divergence of the glass transition can be observed.

Table IV. Swelling Properties of Graft Copolymers with Side Chains of M_n = 11,900

wt % Sty ⇒	39.7	46.5	30.4	23.7
Q (%)	568	548	1368	1250
H (%)	82.4	81.8	92.7	92.0

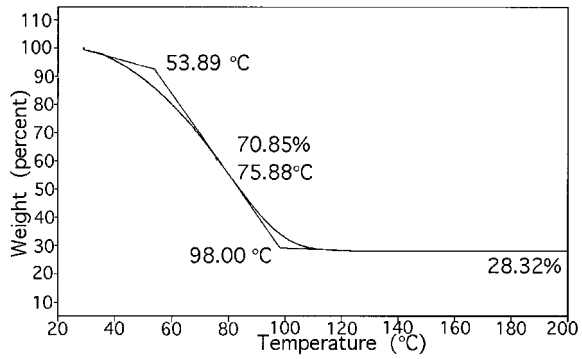

Figure 4. TGA of poly(NVP-*g*-Sty) used to determine water content. Sample shown contains 71% water (H) by TGA and 74% as determined by weight.

Evidence of this problem can be seen from the first two series of copolymerizations with 5800 and 11,900 MW VAc-pSty. For example, there were markedly more of the lower molecular weight grafts incorporated into the copolymer. This was due to the decrease in reactivity of the macromonomers as molecular weight increased and was accentuated by the poor miscibility of polystyrene and poly(*N*-vinyl pyrrolidinone). There was also a substantial decrease in the molecular weight of the copolymer as the size and amount of macromonomer in solution was in-

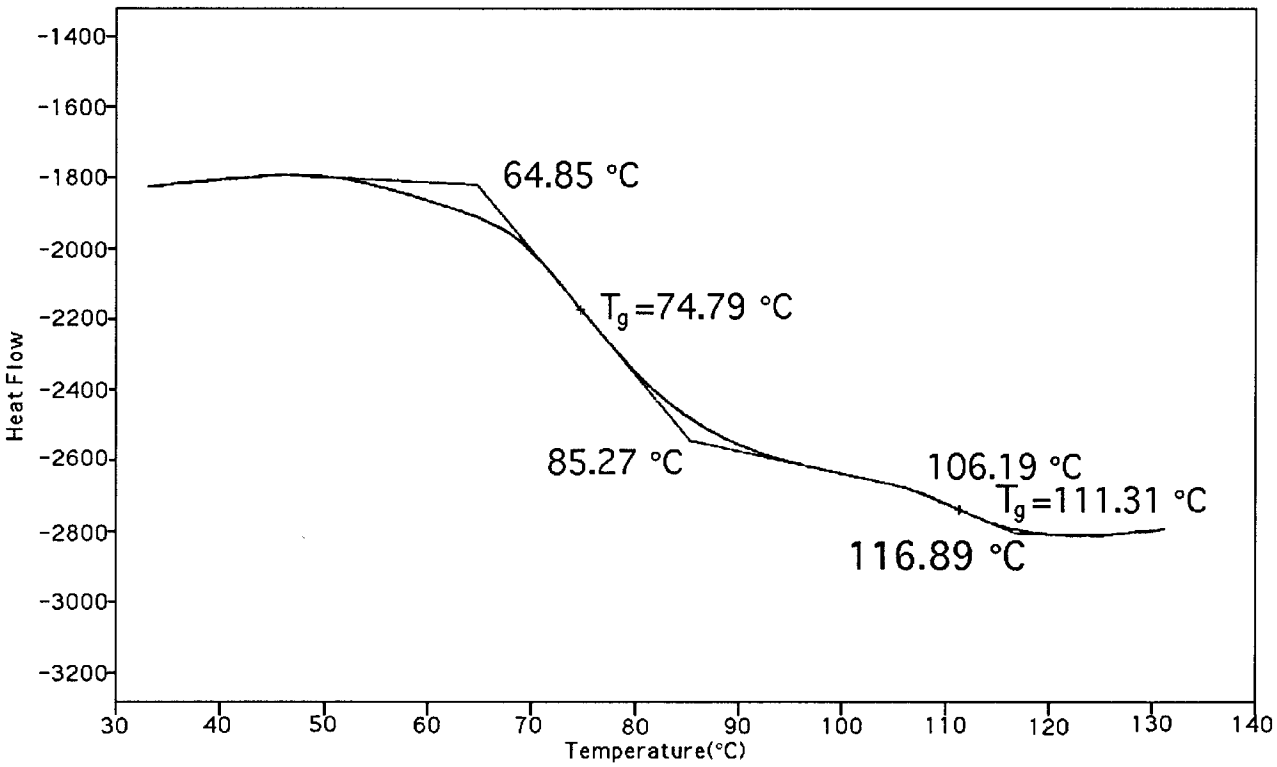

Figure 5. DSC of poly(NVP-*g*-Sty) (M_n = 65,700, PDI = 1.6) showing separate glass transitions corresponding to polystyrene and poly(*N*-vinyl pyrrolidone) segments of the copolymer.

creased. This also implied that there was some heterogeneity to the mixture that limited incorporation of the macromonomer and increased the amount of pNVP homopolymer. Homopolymerization of NVP and limited incorporation of macromonomer, therefore, both contributed to the low yields obtained using the grafting through method.

The swellability of the materials were initially estimated by comparing the mass of dry polymer (W_{dry}) to the swollen polymer (W_{wet}) using the following equations:

$$H = (W_{wet} - W_{dry})/W_{wet} \times 100$$
$$Q = W_{wet}/W_{dry} \times 100 \quad (3)$$

where H is the equilibrium water content and Q is the equilibrium state of swelling (Tables III and IV).[13] The numbers obtained from these calculations were supplemented by thermal gravimetric analysis, which showed the change in mass as water was removed from a swollen sample by heat (Fig. 4). TGA measurements were in agreement with these values within 2–4%. Swelling contents ranged from 74–97% indicating that some of these hydrogels may be a suitable type of material for applications as superabsorbants.

Physical crosslinking of the graft copolymers can be easily seen by changing the solvents used in purifying the solid from one that favors the hydrophilic segments to one that favors the hydrophobic side chains. Precipitation of poly(NVP-*g*-Sty) into water produced a swollen white (or opaque) gel, whereas precipitation into heptane produced a flaky white powder similar to polystyrene homopolymer. In this form, the swollen copolymer has a 20–30% lower water content. For comparison, when the sample containing 40% polystyrene side chains with M_n = 11,900 was precipitated into heptane, dried and allowed to sit in/on water for 1 week, its equilibrium water content was 52.3% and the state of swelling was 210%. In fact, in some cases it repels water, much as regular polystyrene would. From the swollen state, after drying in a vacuum oven, however, the polymer swells almost immediately, reaching equilibrium water content in minutes. Differen-

tial scanning calorimetry analysis of the copolymer also shows separate glass transition temperatures corresponding to transitions of each homopolymer and characteristic of a microphase separated copolymer (Fig. 5).

CONCLUSIONS

ATRP is an effective method for making vinyl macromonomers of polystyrene with narrow polydispersity and molecular weights close to theoretical values based on ratios of monomer to initiator. Using an initiator that contains a double bond for which the propagating radical has a low reactivity produces a homopolymer with an end-functional double bond. The resulting macromonomer can then in theory be copolymerized with any monomer with which the end group would ordinarily be reactive. There are inherent limitations to this method of preparing graft copolymers, however, that are well documented. They include a molecular weight ceiling for the macromonomer, above which the ability to copolymerize is restricted, in addition to a problem with miscibility of monomer and macromonomer, especially in the case of amphiphilic systems such as those studied here.

The ability to alter the physical properties in the poly(NVP-*g*-Sty) copolymers, however, simply by the choice of solvent in precipitation is very interesting. Alternatives to this method are currently under investigation in the lab, including other methods of preparing graft copolymers such as grafting from and other comonomer systems.

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