Synthesis and Copolymerization of Methacryloyl Hydroxamic Acids

GEORGE M. ISKANDER, HEIDI M. KAPFENSTEIN, THOMAS P. DAVIS, DIANNE E. WILEY

School of Chemical Engineering & Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

Received 13 January 1999; accepted 11 January 2000

ABSTRACT: Three methacryloyl hydroxamic acids were prepared and homopolymerized yielding polymers which readily formed complexes with Fe^{3+}. The amount of hydroxamic acid available for complexation was found to be low (29–32% of theoretical). Copolymers of methacryloyl hydroxamic acid with methyl methacrylate were also synthesized. The low amount of free hydroxamic acid functionality in the copolymers was ascribed to transfer reactions in the radical polymerization which resulted in branching and deactivation of the hydroxamic acid functionality. In addition, methacryloyl hydroxamic acid was copolymerized with *N*-isopropyl acrylamide to yield thermotropic polymers capable of complexing with metal ions. At low concentrations of hydroxamic acid functionality, the lower critical solution temperature of the copolymers remained similar to that reported for poly(*N*-isopropyl acrylamide). © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 751–758, 2000

Key words: hydroxamic acid; polymer–metal complexes; branching; transfer; thermotropic

INTRODUCTION

Hydroxamic acid derivatives are known to readily chelate with heavy metals. They have been found to be effective chelating ligands with ions such as V^{5+}, Fe^{3+}, Mo^{6+}, Ti^{4+}, Hg^{2+}, Cu^{2+}, and UO_2^{2+}. A number of studies have shown that hydroxamic acid groups can be incorporated into synthetic polymers to produce a functionalized polymer surface capable of reversibly interacting with metal ions.[1–7] In general, the hydroxamic acid modified resins have been shown to have a 2–7% activity of free hydoxamic acid groups capable of binding to a diverse range of metal ions.

Previous methods used to incorporate hydroxamic acid functionality have involved a postpolymerization reaction step (i.e., a functionalization of the polymer). The maximum level of hydroxamic acid incorporation reported by these postfunctionalization methods is 13%. Kerin and Schultz [2] synthesized polymeric hydroxamic acid by the reaction of poly(methacrylate) and hydroxylamine in benzene. Several other resins containing hydroxamic acid groups have been prepared from Amberlite IRC-50 by conversion of the carboxylic acid to an acid chloride [1] or to an ester [3] followed by treatment with hydroxylamine. Another approach involved the treatment of poly(acrylonitrile) with hydroxylamine followed by the hydrolysis of the resulting hydroxamic acid groups.[4] Poly(acrylic acid) and poly(acrylamide) have also been adopted as starting materials.[5] Hydroxamic acid modified resins based on acrylonitrile–divinyl benzene copolymers have also been reported.[6,7]

The potential utility of these functionalized polymers in membrane applications has also been recognized. Hydroxylamine modified poly(acrylonitrile) ultrafiltration membranes contained amidoximes and hydroxamic acid groups alongside nitrile groups. These polymers were used in ul-

Correspondence to: T. P. Davis.
Contract grant sponsor: Australian Research Council.

Journal of Applied Polymer Science, Vol. 78, 751–758 (2000)

trafiltration membranes and low-pressure reverse-osmosis membranes.[8,9] Other potential applications of polymers for chromatographic separation and porous resin matrices have also been claimed.[10]

Our approach to the present work involved the synthesis of a number of methacryloyl hydroxamic acid (MHDA) monomers which could undergo either homo- or copolymerization with other monomers, thereby expanding the repertoire of host polymers with the aim of increasing the percentage of free hydroxamic acid moieties. Previous work by Agrawal and Rao indicated that this might be a promising synthetic route.[11] An additional aim of this work was to copolymerize the new monomers with *N*-isopropyl acrylamide (NIPAAM) to form thermotropic copolymers capable of complexation to metal ions.

EXPERIMENTAL

Materials

Diethyl ether, toluene, and THF were refluxed over K-*p*-benzoquinone and distilled prior to use. Other solvents were dried over CaH_2, distilled, and stored over molecular sieve 4 Å. Reagents including methacroyl chloride, ethyl 4-hydroxybutanoate, ethyl 6-hydroxyhexanoate, methyl methacrylate (MMA), and NIPAAM were obtained from Aldrich (Castle Hill, NSW, Australia) and used as received. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol prior to use.

Analyses

IR spectra were recorded as liquid films between rock salt plates, or as KBr discs on a Perkin–Elmer (2000 FTIR) instrument. ^{1}H-NMR spectra were recorded on a Bruker AC 300F NMR machine in $CDCl_3$ solvent, unless otherwise stated. Nitrogen was measured by using a Leco CNS-2000 machine at the Australian National University (ANU). Reaction mixtures were examined by thin-layer chromatography (TLC) on Kieselguhr PF 254 plates with ethyl acetate : methanol (5 : 1; v : v) as eluent. GPC analyses were conducted on a modular SEC system, fitted with four fixed pore columns ranging sequentially from 10^3-10^6 Å. The flow rate was maintained at 1 mL/min by using purified HPLC grade THF as carrier solvent and a refractive index detector. As calibration was achieved by using narrow molecular weight poly(styrene) and poly(methyl methacrylate) standards, the final molecular weight data are subject to inaccuracies.

Monomer Syntheses

Preparation of Methacryloyl Hydroxamic Acid (MHDA) (I)

This hydroxamic acid monomer was conveniently prepared from the acid chloride, methacroyl chloride (10.45 g, 0.11 mol), being added dropwise over 45 min to an ice-cooled and stirred mixture of hydroxylamine hydrochloride (7.65 g, 0.11 mol), NaOH (9.2 g, 0.23 mol), water (35 mL), and diethyl ether (80 mL). Small amounts of hydroquinone (0.05 g) and tetrabutyl ammonium bromide (0.1 g) were added. The mixture was stirred for 3 h at 0°C and then left to stand overnight in the refrigerator. Subsequently, the mixture was acidified with HCl (35%) to pH 5.0; the organic phase separated out, and the aqueous phase extracted twice with ether (50 mL total). The combined ethereal phase was dried (Na_2SO_4), and the solvent evaporated *in vacuo*. The pale-yellow liquid obtained initially solidified to a waxy solid (8.24 g; 81.54%), m.p. 38–40°C. The compound proved to be a trihydrate from ^{1}H-NMR (broad signal at δ 5.15) and from nitrogen analysis: N (9.205%; $C_4H_{13}NO_5$ requires N, 9.03%). IR: ν_{max} (Nujol) 3208, (—OH str), 1652 (C═O, str), 1634, 1520, 1456, 1377, 1837, 1294, 1243, 1221, 1148, 1121, 1039, 953, and 900 cm^{-1}. ^{1}H-NMR: δ 10.2 (br s, 2 h, —N*HOH*), 6.3 (s, 1 h, ═CH_2), 5.3 (s, 1 h, ═CH_2), and 2.0 (s, 3 h, —CH_3).

Preparation of 4-Hydroxybutanoyl Hydroxamic Acid

Ethyl 4-hydroxybutanoate (13.22 g; 0.1 mol) was added to a solution of hydroxylamine hydrochloride (13.9 g, 0.2 mol) and NaOH (12 g, 0.3 mol) in water (30 mL). The stirred mixture was heated at 70°C overnight, then cooled and acidified to a pH of 4.0. The clear aqueous solution was evaporated nearly to dryness *in vacuo*, and the residual solids were extracted with THF (five times, 150 mL total). The solution was filtered through celite and evaporated *in vacuo*, leaving a colorless semisolid (5.09 g; 42.8%). Colorless needles were obtained from THF, m.p. 114–115°C.

IR: ν_{max} 3243 (OH str), 1661 (C═O str), 1539, 1426, 1372, 1323, 1261, 1206, 1032, and 977 cm^{-1}. ^{1}H-NMR: δ 10.0 (br s, 1H, —NHO*H*),4.35 (m, 1H, —NH), 3.0–3.5 (m, 1H, —OH), 2.5 (m, 2H, —CH_2CO—), 1.8–2.0 (m, 2H, —CH_2OH), and 1.35 (d, 2H, —CH_2).

6-Hydroxyhexanoyl Hydroxamic Acid

6-Hydroxyhexanoyl hydroxamic acid was prepared from the corresponding ester as above (91%). A portion was distilled at bp 150°C/0.05 mmHg, which solidified on standing overnight in the refrigerator; m.p. 55.7°C.

IR ν_{max} 3213 (—OH str), 1644 (C═O str), 1459, and 1051 cm^{-1}. ^{1}H-NMR: δ 10.0 (br s, 1H, —N*H*OH), 3.62–4.40 [m, 2H, —NH and — $(CH_2)_5$—*OH*], 2.25–2.55 (m, 2H, —CH_2CO—), and 1.30–1.95 (m, 8H, 4 CH_2's chain).

Methacryloylbutanoyl Hydroxamic Acid (MBHDA) (II)

Methacroyl chloride (5.37 g, 0.055 mol) was added dropwise (ca. 0.5 h) to a stirred, ice-cooled solution of 4-hydroxybutanoyl hydroxamic acid (5.95 g, 0.05 mol) in a mixed solvent of THF (40 mL) and ether (40 mL); triethylamine (7.6 g, 0.075 mol) was added. The mixture was stirred for a further 12 h at room temperature. It was then acidified with a few drops of concentrated HCl to pH 4.0; a white solid precipitated (Et_3NHCl). The organic phase was separated, and both the aqueous phase and the solids were extracted with THF (five times, 200 mL total). The solution was filtered through celite and evaporated *in vacuo*, leaving a pale-yellow syrup, which solidified to a waxy solid by standing overnight in the refrigerator (9.0 g; 96.3%). The solid was washed twice with Et_2O giving a white solid, m.p. 78.6°C. R_F, 0.45.

IR: ν_{max} 3272 (—OH str), 1716 (C═O, str), 1636, 1455, 1378, 1297, 1156, 1085, C—O—, str), 948, and 803 cm^{-1}. ^{1}H-NMR: δ 10.0 (br s, 1H, —NHO*H*), 6.35 (d,1H, ═CH_2), 5.85 (d, 1H, ═CH_2), 4.30 (m, 1H, —NH), 2.45 (m, 4H, methylene H, s), 2.05 (t, 2H, —OCH_2), and 1.35 (d, 3H, Me).

Methacryloylhexanoyl Hydroxamic Acid (MHHDA) (III)

MHHDA was prepared as above from the corresponding 6-hydroxyhexanoylhydroxamic acid (90%) as a pale-yellow thick oil.

IR: ν_{max} 3170 (—OH str), 1710 (C═O str), 1633, 1450, 1376, 1290, 1150, 945, and 805 cm^{-1}. ^{1}H-NMR: δ 10.0 (brs, 1H, —NHO*H*), 6.38 (d, 1H, ═CH_2), 5.70 (d, 1H, ═CH_2), 4.2 (m, 1H, —N*H*—), 3.60 (m, 2H, —CH_2—OCO—), 2.20 (m, 2H, —CH_2CO—), and 1.30–2.00 (m, 9H, —CH_3, and 3CH_2, chain).

Polymer Syntheses

Poly(methyl methacrylate) (PMMA)–Hydroxamic Acid: Modification of PMMA

PMMA (Scientific Polymer Products) (M_n, 33,200; P_D, 1.82) (5.0 g) was suspended in methanol (200 mL); sodium methoxide (4.46 g, 0.083 mol) and hydroxylamine hydrochloride (5.21 g, 0.075 mol) were added, and the mixture was heated under reflux, with stirring for 24 h. The reaction mixture was cooled, and the polymer was filtered and washed with dilute HCl (1*M*) and water until the washings were neutral (pH 7). The polymer was then washed with methanol and diethyl ether and dried (5.0 g).

Homopolymerizations of MHDA and MBHDA

The monomer (ca. 1 g) was dissolved in dry toluene (20 mL); AIBN (0.03 g; 0.15%) was added and the solution was degassed by two freeze–thaw cycles. The solution was heated at 60°C for 4 h, then cooled and added to a large volume of *n*-hexane. The polymer was isolated, redissolved in a minimal amount of chloroform, and reprecipitated by addition to an excess of methanol. It was then filtered and dried.

Copolymerizations of MHDA with MMA and NIPAAM

Comonomer solutions containing AIBN and 1, 2, and 4 wt % MHDA were charged to glass ampoules. The solutions were degassed by two freeze–thaw cycles and heated at 60°C for 3–6 h. After cooling, the mixture was poured into a large volume of methanol and the precipitated polymer was collected and dried. Copolymers of MHDA and NIPAAM were prepared in a similar fashion.

Estimation of Free Hydroxamic Acid in The Polymers

An estimate was made of the free hydroxamic acid functionality in the polymers by measuring the extinction coefficient of the complex formed by the relevant monomer and Fe^{3+} at 526 nm. It is known that monohydroxamic acids form octahedral complexes with Fe^{3+} via the two oxygen atoms of the deprotonated hydroxamic acid group.[12] The use of spectrophotometric assay for the quantitative determination of hydroxamic acid functionality has been used for small molecule hydroxamic acid derivatives.[13] The polymer-bound hydroxamic acid was assumed to have the same extinction coefficient as the corresponding mono-

mer. Some errors are possible in the approach as the Beer–Lambert law assumes no specific molecular interactions: this assumption cannot be verified the in this particular case. However, we believe that the results from this type of analysis should provide some insight into the approximate level of hydroxamic acid available for complexation.

Measurement of Transfer to Monomer and Propagation Rate Coefficients

The transfer to monomer coefficient, C_s, and the propagation rate coefficient, k_p, were determined by using the chain-length distribution method (CLD) and pulsed-laser polymerization (PLP), respectively.

Chain-Length Distribution

The polymerizations were performed in 20-mL sealable flasks. A stock solution of AIBN ($\sim 10^{-2}$ mol L^{-1}) in monomer was prepared. Successive dilutions of the stock solution yielded a series of solutions with different initiator concentrations. The solutions were deoxygenated by purging with argon for 10 min prior to polymerization. Polymerizations were performed at 60°C in a constant temperature water bath and the reactions stopped by cooling in an ice bath followed by the addition of hydroquinone. All conversions were $<5\%$.

Pulsed-Laser Polymerization

Purified monomers and AIBN were weighed into Pyrex sample tubes (10 mm diameter by 60 mm height), which were then sparged by bubbling with nitrogen for 5 min and sealed with rubber septa. The reaction mixtures were equilibrated at the reaction temperature prior to laser exposure. The polymerizations were initiated by a pulsed Nd:YAG laser (Continuum Surelite I-20) with a harmonic generator (a Surelite SLD-1 and SLT in series), which was used to produce the 355-nm UV laser radiation, and a wavelength separator (Surelite SSP-2), which was used to isolate the 355-nm beam. The laser beam was directed at a constant pulsing rate through the sensitized monomer solution. The frequency of the flash lamp discharge, measured at 19.96 ± 0.04 Hz using a photodiode in conjunction with an oscilloscope, was controlled by a software oscillator, and the Q-switch (and thus the laser) was pulsed at various fractions of this rate, as set by a software divider function. During the polymerizations, the sample was held in a thermostated copper cell. Chain growth was terminated by removing the sample from the laser and precipitating the polymer. The polymer was then isolated, further purified of residual monomer via a redissolution–reprecipitation technique, and then dried to constant mass *in vacuo* at 40°C.

Determination of Lowest Critical Solution Temperatures (LCST) for NIPAAM/MHDA Copolymers

The LCSTs of the copolymers of MHDA with NIPAAM, in water (0.1 wt %) were measured by using a Jasco-5055 V-530 UV–Vis spectrophotometer at a fixed wavelength of 550 nm. The absorbance of the solution was monitored on heating from 20 to 40°C at 1°C/min. The reversibility of the LCST was monitored for these solutions by cooling from 40 to 20°C.

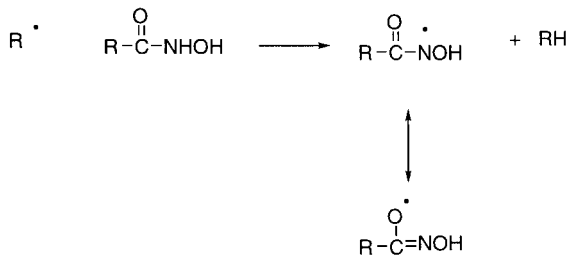
RESULTS AND DISCUSSION

Modification of PMMA

As indicated in the experimental section, PMMA was modified via reaction with hydroxylamine hydrochloride, following a previously reported method. In the previous work, the total hydroxamic acid present in the polymer was verified by chemical analyses. However, it seems that a verification of the free hydroxamic acid functionality available for complexation has not been estimated previously. In this work, an estimation of the hydroxamic acid functionality was made by forming a complex between the hydroxamic groups and Fe^{3+} and monitoring the UV absorbance of the complex at λ_{max} (around 526 nm). Both the ^{1}H-NMR (CCl_4) (δ 6.2–7.5, br) and the UV absorption of the Fe(III) complex revealed the presence of —NHOH function estimated at ca. 1.0–1.6%.

Homopolymerizations of MHDA and MBHDA

The polymerizations of MHDA and MBHDA were subject to induction time periods that indicated some inhibition of the polymerization. This may possibly be attributed to a reaction between primary radicals and the hydroxamic acid functionality producing relatively stable radicals, as shown in **Scheme 1**. The UV–Vis spectra were calibrated by measuring the extinction coefficient of the MHDA and MBHDA monomers complexed with Fe^{3+}, as detailed in the experimental section. Applying these extinction coefficients to the



Scheme 1 Possible mechanism of transfer to the hydroxamic acid functionality causing initial induction times and transfer to monomer and polymer.

respective homopolymers indicated relatively low active hydroxamic acid functionality, as shown in Table 1.

It is obvious from the data shown here that a fairly significant amount (ca. 70%) of the hydroxamic acid groups remain inactive toward complexation with Fe(III) and therefore undetected by UV–Vis spectroscopy. One explanation for these results is that transfer reactions to polymer and/or monomer cause a loss of hydroxamic functionality via a route similar to that depicted in **Scheme 1**. This was investigated further by studies on the copolymerization of MHDA with MMA.

Copolymerization of MHDA with MMA

Samples of MHDA/MMA copolymers containing low concentrations of hydroxamic acid were analyzed by UV–Vis spectrophotometry as Fe(III) complexes and also for total nitrogen content by elemental analysis. The results are shown in Table 2.

It is clear that not all of the MHDA retains the active hydroxamic acid functionality when it is incorporated in the copolymer. As with the homopolymerizations, one possible explanation is that some hydroxamic acid groups are involved in transfer reactions, both transfer to monomer and transfer to polymer, following a similar reaction path to that described in **Scheme 1**. As measurements on transfer to polymer are difficult, we elected to concentrate our initial efforts of measuring the transfer to monomer at low conversion. In the following section, we describe measurements of chain transfer to monomer and propagation rate coefficients for the copolymerization of MMA with MHDA (10 vol %).

Table I Free Hydroxamic Acid in the Homopolymers of PMHDA and PMBHDA Measured Using UV–Vis Absorbance of the Hydroxamic Acid–Fe^{3+} Complex

Polymer	Wavelength (λ_{max})	Concentration (% Theoretical)
PMHDA	526.17	32.215
PMBHDA	526.17	29.491

Table II Concentrations of Hydroxamic Acid in Copolymers of MMA and MHDA

% Hydroxamic Acid (theory)[a]	Total % Hydroxamic Acid Found[b]	Measured % Free Hydroxamic Acid[c]
4.0	1.49	1.19
2.0	0.71	0.20
2.0	0.50	0.19

[a] Calculated from the MHDA monomer feed concentration.
[b] Calculated on the basis of Kjeldahl nitrogen analysis.
[c] Calculated on the basis of UV–Vis spectroscopy of the hydroxamic acid–Fe^{3+} complex.

Measurement of Transfer to Monomer in the Copolymerization of MHDA with MMA

The CLD approach has recently been developed by Gilbert and coworkers,[14] founded on the idea that chain-length effects on termination diminish if one determines the high-molecular-weight slope of a molecular weight distribution which is plotted as the natural logarithm of the number distribution, $P(M)$, versus molecular weight:

$$\lim_{M\to\infty} P(M) = \text{constant} \times \exp\left(-\frac{\langle k_t\rangle[R^\bullet] + k_{tr}[M]}{k_p[M]}\frac{M}{m_0}\right) \quad (1)$$

where $P(M)$ is the number of chains of molecular weight M, m_0 is the molecular weight of monomer, $[M]$ and $[R^{[\text{chempt}]}]$ are the monomer and radical concentrations, respectively, k_{tr} and k_p are the rate coefficients for chain transfer to monomer and propagation, respectively, and $\langle k_t\rangle$ is the average termination rate coefficient. As the concentration of initiator is reduced, the radical concentration, and hence the rate of termination, decreases. This eventually leads to the termination rate being insignificant compared to the chain transfer rate and so $\langle k_t\rangle[R^{[\text{chempt}]}] \ll k_{tr}[M]$, allowing eq. (1) to be simplified as:

$$\lim_{M\to\infty,[I]\to 0} P(M) = \text{constant} \times \exp\left(-C_M\frac{M}{m_0}\right) \quad (2)$$

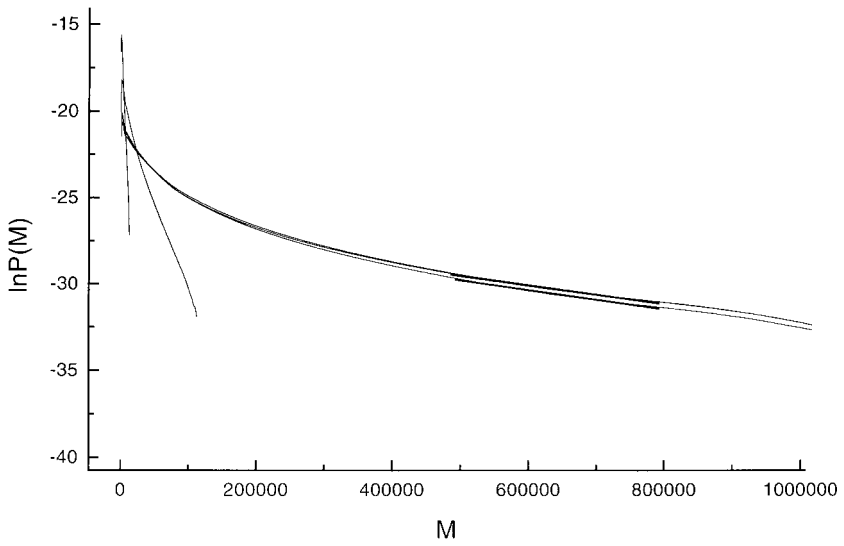


Figure 1 The ln $P(M)$ versus M plots for the copolymerization of MMA with 10 wt % MHDA.

Thus in the limit of low initiator concentration, the chain transfer to monomer constant, C_M ($=k_{tr}/k_p$), can be determined from the slope of the molecular weight distribution, plotted as ln $P(M)$ versus M.

The ln $P(M)$ versus M plots for the copolymerization of MMA with 10 wt % MHDA are shown in Figure 1, yielding a value for the C_M of 5.5×10^{-4} at 60°C. This value may be compared with a literature value for MMA of 5.15×10^{-5} at 50°C.[15] Clearly, the MHDA has a substantial influence on the reaction. However, it is not possible on the basis of this analysis alone to unequivocally ascribe the C_s value to transfer, as the effect may be in the propagation rate coefficient. To test this, we performed a PLP experiment to determine k_p for this copolymerization.

Pulsed-Laser Polymerization

The technique of PLP is now firmly established for measuring k_p values.[16] Two SEC chromatograms showing molecular weight distributions obtained from the PLP experiments on the copolymerizations of MMA with 1 and 10% MHDA are shown in Figure 2. It is evident from these traces that the increased concentration of MHDA broadens the molecular weight distribution and the characteristic features of a typical PLP distribution are becoming less pronounced; this is strongly indicative of a transfer process. The experiments were conducted at 20 Hz and 60°C, yielding a $\langle k_p \rangle$ value of 820 L mol^{-1} s^{-1}, which can be compared to a reported value of k_p for MMA of 831 L mol^{-1} s^{-1} at the same temperature.[17] Thus it is evident that the MHDA (10%) has a minimal effect on the propagation rate, so the order of magnitude increase in the C_s value can be solely attributed to a large increase in the transfer rate.

All of these kinetic measurements were made at low conversion. At higher conversions, it is likely that transfer to hydroxamic groups in the polymer also occurs, resulting in extensive branching and crosslinking. Therefore it seems likely that transfer reactions cause a reduction in the active hydroxamic acid concentration in the polymer. This is a limitation of the utility of these hydroxamic acid monomers for synthesizing resins with high complexation capacity and explains why the homopolymers of these monomers yield quite low free hydroxamic acid groups for complexation (*vide infra*).

Copolymerization of MHDA with NIPAAM

Several additional experiments were performed to investigate the possibility of forming thermotropic copolymers, capable of complexing to metal ions by the copolymerization of the MHDA with NIPAAM. In these MHDA/NIPAAM copolymers, the amount of free hydroxamic acid available for complexation is significantly less than that we would predict from the monomer feed ratios, as shown in Table 3. Some of this reduction may be ascribed to incomplete polymerization (conversion was approximately 80%); however, it is likely that some reduction in complexation efficiency is again caused by the deactiva-

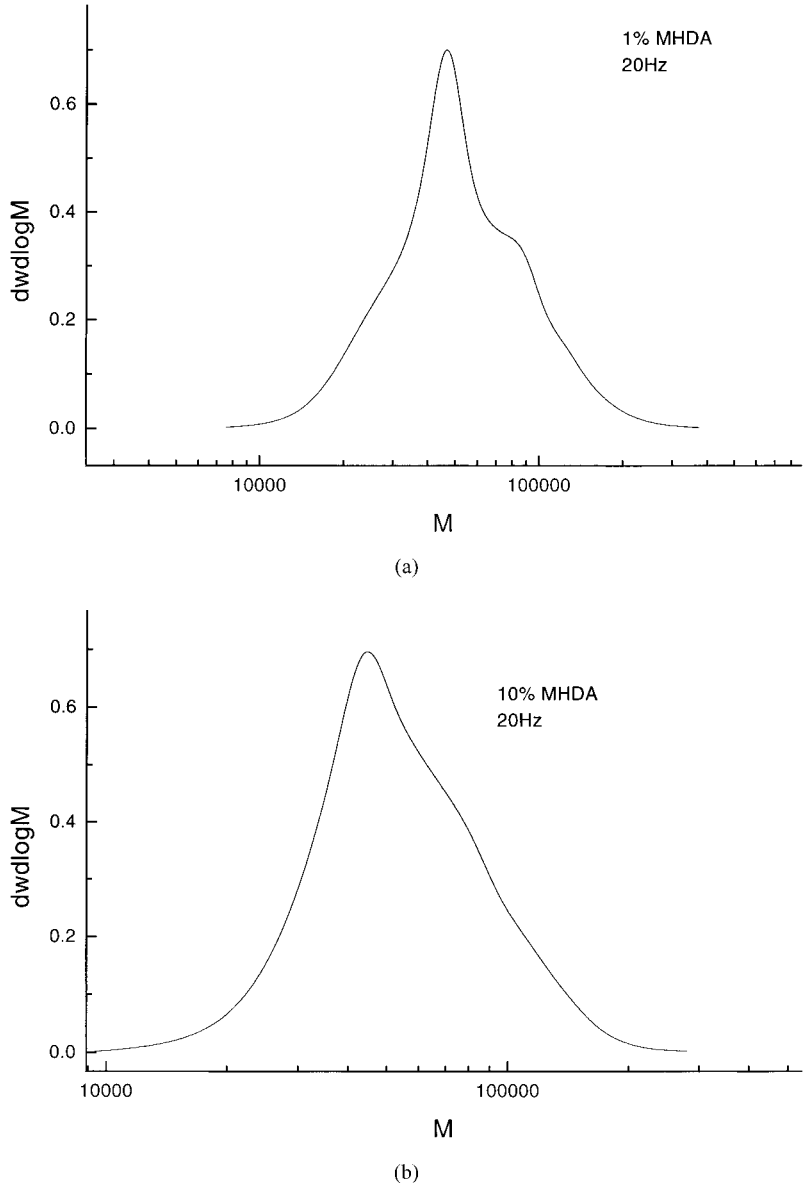


Figure 2 Molecular weight distributions from the pulsed-laser polymerizations of (a) MMA + 1% MHDA at 20 Hz and (b) MMA + 10% MHDA at 20 Hz.

tion of the hydroxamic acid functionality resulting from radical transfer reactions.

The LCSTs of the MHDA/NIPAAM copolymers were measured by turbidity experiments and are shown in Table III. A typical trace obtained from UV–Vis spectrophotometry is shown as Figure 3. At low levels of incorporation of free MHDA, we found that the LCST of the copolymers was very similar to that reported previously for PNIPAAM.[18]

CONCLUSION

In this work, we showed that it is possible to introduce hydroxamic acid functionality to polymers by

Table III Concentration of Free Hydroxamic Acid in the MHDA/NIPAAM Copolymers

% MHDA in Comonomer Feed	% Free Hydroxamic Acid in Copolymer[a]	LCST (°C)
2	1.41	31–33
4	2.96	32–33
6	2.97	32–33
8	3.39	33–34
10	5.21	33–34

[a] Calculated on the basis of UV–Vis spectroscopy of the hydroxamic acid–Fe^{3+} complex.

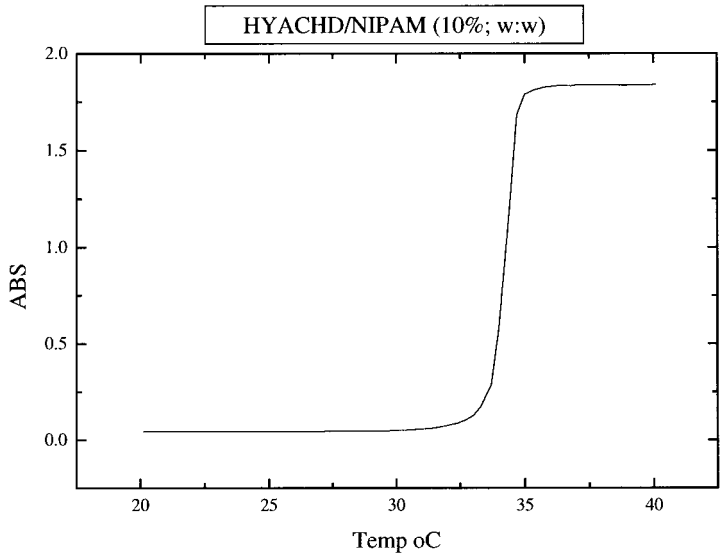


Figure 3 Turbidity trace showing the LCST of a copolymer of NIPAAM/MHDA containing 5.21% active hydroxamic acid functionality.

synthesizing methacryoyl hydroxamic acid monomers which undergo free radical homo- and copolymerization. However, the hydroxamic acid functionality provides a labile hydrogen which causes both inhibition and transfer with the result of reducing the overall free or active hydroxamic acid available for complexation with metal ions. Despite this problem, it is possible to synthesize potentially useful polymers capable of acting as complexing agents. Finally, this work shows the potential for utilizing hydroxamic acid functionality in thermotropic polymers. The judicious selection of pH conditions may well allow for selective complexation, permitting the separation of specific metal ions from a mixture by using either membranes or ion exchange resins based on these polymers.[19]

We thank the Australian Research Council for funding (DEW, TPD) and acknowledge the provision of an Australian Postgraduate Award (to HMK).

REFERENCES

1. Crumbliss, A. L.; Garrison, J. M. Inorg Chim Acta 1987, 133, 281.
2. Kerin, W.; Schultz, R. C. Angew Chem 1957, 69, 153.
3. Petrie, G.; Locke, D.; Meloan, C. E. Anal Chem 1965, 37, 919.
4. Schoulteden, F. Makromol Chem 1958, 27, 246.
5. Domb, J.; Carvalho, E. G.; Langer, R. J Polym Sci, Polym Chem Ed 1988, 26, 2623.
6. Vernon, F.; Eccles, H. Anal Chim Acta 1975, 77, 145.
7. Vernon, F. Pure Appl Chem 1982, 54, 2151.
8. Lee, T. S.; Hong; S. I. Polym Bull 1994, 32, 273.
9. Lee, T. S.; Hong, S. I. J Polym Sci, Polym Chem Ed 1995, 33, 203.
10. Kamble, K. J.; Patkar, D. N. J Appl Polym Sci 1994, 52, 1361.
11. Agrawal, Y. K.; Rao, K. V. React Funct Polym 1996, 31, 225.
12. Kurzak, B.; Kozlowski, H.; Farkas, E. Coord Chem Rev 1992, 114, 169.
13. Fournand, D.; Pirat, J.-L.; Bigey, F.; Arnaud, A.; Galzy, P. Anal Chim Acta 1997, 353, 359.
14. Christie, D. I.; Gilbert, R. G. Makromol Chem Phys 1996, 197, 403.
15. Kukulj, D.; Davis, T. P.; Gilbert, R. G. Macromolecules 1998, 31, 994.
16. Coote, M. L.; Zammit, M. D.; Davis, T. P. Trends Polym Sci 1996, 4, 189.
17. Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Olaj, O. F.; Russell, G. T.; Schweer, J.; van Herk, A. M. Macromol Chem Phys 1997, 198, 1545.
18. Schild, H. G. Prog Polym Sci 1992, 17, 163.
19. Beauvais, R. A.; Alexandratos, S. D. React Polym 1998, 36, 113.