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A new polymer with a lower critical solution temperature: poly(α-methoxymethyl acrylic acid)

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A new monomer and its water-soluble polymer have been synthesized containing pendant methyl ether and carboxylic acid groups. This polymer was found to possess a lower critical solution temperature (LCST) in pure water that is dependent on added salt and almost independent of polymer concentration (above 3×10^{-4} wt.%). Values of the LCST typically ranged from around 40–50°C but decreased to 35°C in 1% NaCl. © 1998 Elsevier Science Ltd.

(Keywords: lower critical solution temperature; *t*-butyl α-hydroxymethyl acrylate; poly(α-methoxymethyl acrylic acid))

Introduction

Most α-alkyl substituted acrylates in which the α-substituent is larger than a methyl group polymerize poorly[1]. However, it has been shown that α-substituted acrylates which contain heteroatoms in the position β to the carbon–carbon double bond will readily polymerize to high molecular weight polymers[2]. One such polymer, poly(α-methoxymethyl acrylic acid) (pMMAA) has been found to display a lower critical solution temperature (LCST)[3].

The LCST is an unusual phenomenon in that solubility decreases with increasing temperature. This arises from the loss of mobility that a solvent molecule undergoes when interacting with a macromolecule; *i.e.* the loss of entropy associated with the solvent–polymer interaction is compensated for by a favourable energy of mixing. However, as the temperature increases, $T\Delta S$ becomes more unfavourable until it overbalances the enthalpic term. At this temperature (the LCST), phase separation occurs, and the solution gels or the polymer precipitates.

One well-characterized polymer showing this behaviour is poly(*N*-isopropyl acrylamide), for which Heskins and Guillet[4] measured an LCST of 32°C in aqueous solution. Others have explored using this polymer's LCST ability to fashion smart materials for artificial muscles[5–7].

The LCST behavior of pMMAA is described here with regard to the variation of the cloud point for several samples (with various molecular weights) with respect to concentration and added salt.

Experimental methods, results and discussion

The synthetic scheme for pMMAA (*Figure 1*) involves *tert*-butyl α-hydroxymethyl acrylate (*t*-BHMA), synthesized with use of a procedure similar to that described by Bittman and co-workers for ethyl α-hydroxymethyl acrylate[8]. Water (100 ml), paraformaldehyde (33 g, 1.1 mol), and 4 ml of 1 N *o*-phosphoric acid were stirred for 1.5 h at 80°C to form a colourless aqueous formaldehyde solution. THF (100 ml), *tert*-butyl acrylate (140 ml, 0.96 mol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (11.3 g, 0.101 mol) were added. The mixture was stirred for 2 days at 80°C. NaCl (35 g) and 100 ml of diethyl ether were added. The aqueous layer was separated and extracted three times with 100 ml portions of ether. The combined organic layers were washed twice with 100 ml portions of saturated aqueous NaCl. The organic layers were dried over $MgSO_4$ and filtered. After the addition of $CuCl_2$ as a free radical inhibitor, the solvents were evaporated. Vacuum distillation gave 48.5 g of 96% pure *t*-BHMA (28% yield), and the structure was confirmed by ^{13}C n.m.r.

Conversion to *tert*-butyl α-bromomethylacrylate involved reaction with PBr_3[2]. *t*-BHMA (25 g, 0.158 mol) and 100 ml of ether were mixed in a three-necked round-bottomed flask equipped with a reflux condenser, with magnetic stirring under a nitrogen atmosphere, and the mixture was cooled to 0°C by use of an ice bath. PBr_3 (45 g, 0.18 mol) was added dropwise via an addition funnel to prevent overheating of the reaction mixture. After the addition, the mixture was allowed to attain room temperature and was stirred for 3 h before washing with water. The aqueous layers were back extracted with CH_2Cl_2, and the organic layers were dried over $MgSO_4$ and filtered. The solvents were removed by evaporation, and vacuum distillation gave *t*-BBMA (20 g, 56.9% yield).

Synthesis of *tert*-butyl α-methoxymethyl acrylate (*t*-BMMA)[3] was readily achieved by subsequent reaction with methanol[9]. *t*-BBMA (21 g, 0.097 mol) was mixed with methanol (11.8 ml, 0.291 mol) in a 100 ml round-bottomed flask cooled to 0°C. Triethylamine (TEA) (40 ml, 0.289 mol) was added via an addition funnel. The mixture was then heated in an oil bath to 60°C. After 10 h, 50 ml of ether and 50 ml of hexane were added to the reaction mixture, which was then washed twice with 50 ml portions of 1% aqueous HCl. The aqueous layers were combined and back extracted with 50 ml of CH_2Cl_2. The combined organic layers were dried with $MgSO_4$ and filtered. $CuCl_2$ was added and the solvents were removed by rotary evaporation. Vacuum distillation gave 98% pure *t*-BMMA (11 g, 66% yield). *t*-BMMA was then polymerized in bulk at room temperature with 0.5 wt.% 2,2′-azobisisobutyronitrile (AIBN)[10].

Deprotection of poly(*t*-BMMA) was accomplished by placing 2 g of polymer and 20 ml of trifluoroacetic acid (TFA) in a round-bottomed flask equipped with a magnetic

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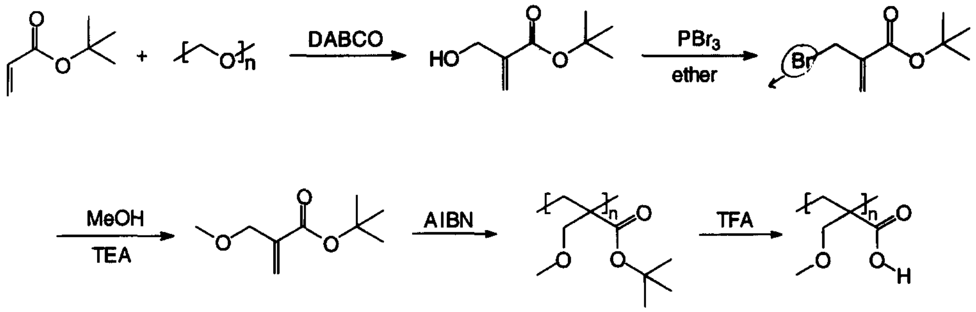

Figure 1 Synthetic scheme for poly(α-methoxymethylacrylic acid)

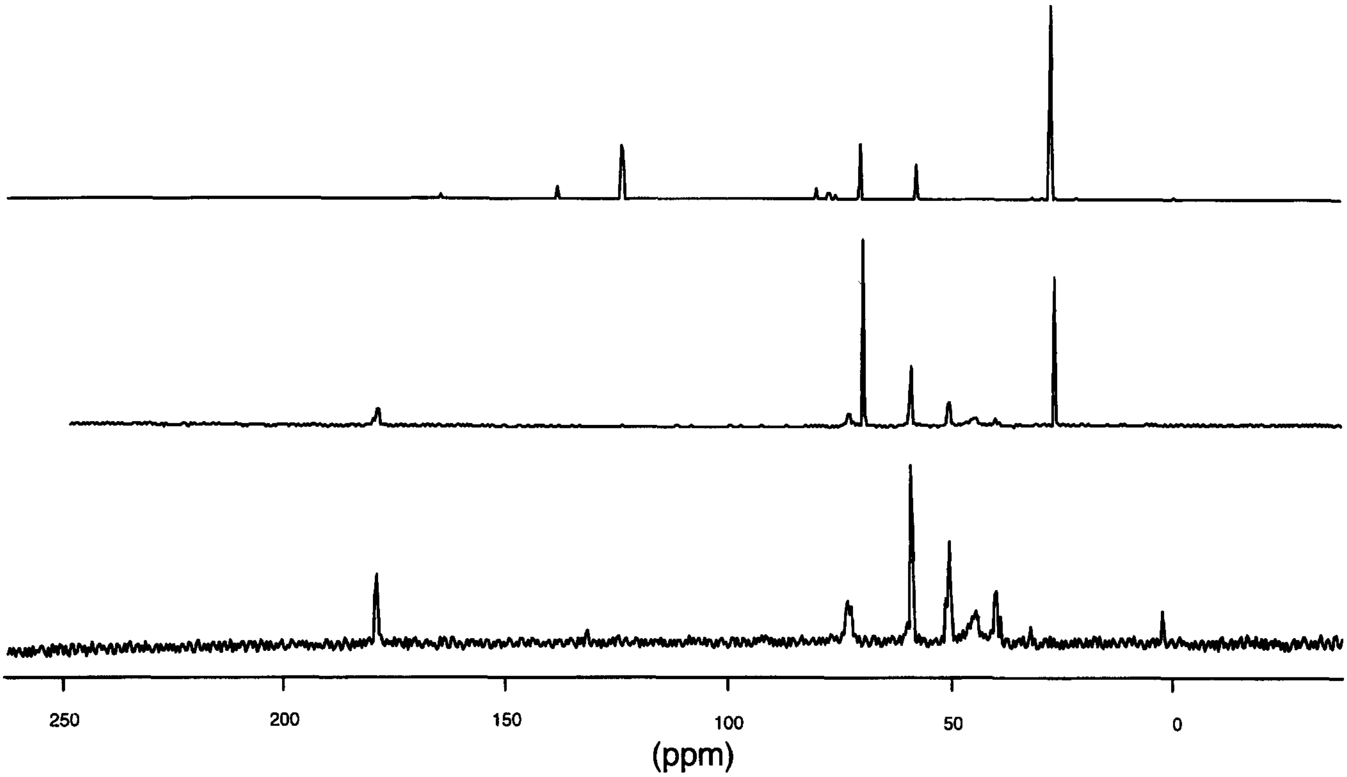

Figure 2 ^{13}C n.m.r. spectra for (top) *t*-BMMA, (middle) poly(*t*-BMMA), and (bottom) pMMAA

stir-bar. The mixture was stirred for at least 24 h at room temperature. TFA was then removed by rotary evaporation. The remaining solid was dissolved in water, and the solution was again subjected to partial rotary evaporation to remove any remaining TFA. The solution was then freeze-dried to give purified deprotected polymer. In an alternative procedure, poly(*t*-BMMA) was deprotected in the same manner, and purified by removing the TFA by rotary evaporation, dissolving the remaining solid in deionized water and precipitating into acetone. The ^{13}C n.m.r. spectra for *t*-BMMA, poly(*t*-BMMA), and pMMAA are shown in *Figure 2*.

The deprotected polymer was dissolved in deionized water, and solutions were prepared in concentrations of 0.01–0.15 g pMMAA per gram of water. Samples of the solutions were placed in capillary tubes and the cloud points were measured visually using a melting point apparatus. The minima of the curves thus obtained were taken to be the LCSTs of the polymers. The LCST was measured in the same manner for pMMAA in 1% $NaCl_{(aq)}$.

The molecular weight for poly(*t*-butyl α-methoxymethyl acrylate) was as high as $M_n = 105\,000$; $M_w = 170\,000$ (SEC estimates[11]) when the monomer purity approached 100%. However, small amounts of impurities often limited M_n to 40 000–50 000 and M_n to 100 000–112 000. This is somewhat lower than has been found for many other β-heteroatom-containing acrylate monomers, which generally polymerize to weights of several hundred thousand to millions. These lower molecular weights are attributable to chain transfer[9,12] which is especially evident for ether derivatives of α-hydroxymethyl acrylates due to the stability of the allyl alkoxy radicals formed[12]. Chain transfer was minimized here by carrying out the polymerizations at room temperature, which lowered the amount of transfer relative to propagation. Polydispersities ranged from 1.6 to 2.2 and SEC showed single-peak traces, indicating an absence of autoacceleration.

When poly(*t*-BMMA) was deprotected with trifluoracetic acid, nearly 100% of the *t*-butyl groups were cleaved to form free acids, as shown by the disappearance of the peak at 26.7 ppm (methyl groups of the *t*-butyl ester). The deprotection was carried out at room temperature because

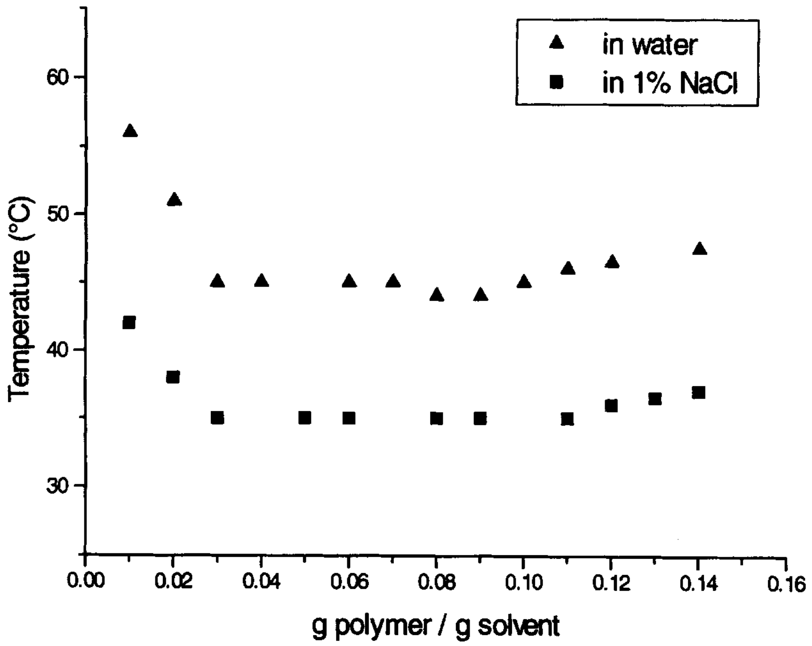

Figure 3 LCST curves for pMMAA in H_2O and in 1% $NaCl_{(aq)}$

reaction at higher temperatures resulted in insoluble products, presumably due to the formation of anhydride cross-links.

The cloud points of aqueous solutions of pMMAA (estimated $M_n = 70\,000$; $M_w = 114\,000$) at various concentrations are shown in *Figure 3*. The LCST was 45.0°C at a critical concentration of 0.03 g polymer per gram of water. In 1% aqueous NaCl, the LCST was 35.0°C over a broad polymer concentration range. Above the critical values, the LCST remained fairly constant with respect to molecular weight and concentration of polymer.

Conclusions

A new polymer possessing a combination of pendant acid and ether groups on every repeat unit has been discovered to display LCST behaviour near room temperature. Deprotection using TFA provides a facile method of synthesizing such carboxylic acid-containing polymers from *t*-butyl ester precursor polymers under relatively mild conditions and in nearly complete conversion. A more thorough investigation is under way with regard to the LCST behaviour of pMMAA-based copolymers, and pMMAA in the presence of additives such as surfactants and other ionic salts.

Acknowledgements

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References

1. Penelle, J., Collot, J. and Ruffland, G., *J. Polym. Sci. Part A: Polym. Chem.*, 1993, **31**, 2407.
2. Reed, S. F. and Baldwin, M. G., *J. Polym. Sci.*, 1963, **1**, 1919.
3. Mathias, L. J., Thompson, R. D. and Michalovic, M., *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, 1995, **36(1)**, 114.
4. Heskins, M. and Guillet, J. E., *J. Macromol. Sci.-Chem.*, 1968, **A2(8)**, 1441.
5. Shibyama, M., Morimoto, M. and Nomura, S., *Macromolecules*, 1994, **27**, 5060.
6. Inomota, H., *Macromolecules*, 1994, **27**, 6459.
7. Mueller, K. F., *Polymer*, 1993, **33(16)**, 3470.
8. Byun, H. S., Reddy, K. S. and Bittman, R., *Tetrahedron Lett.*, 1994, **35**, 13719.
9. Thompson, R. D., Barcaly, T. B., Basu, K. B. and Mathias, L. J., *Polym. J.*, 1995, **27**, 32512.
10. Polymerization was carried out by placing *t*-BMMA (1.0 g) in a test tube with AIBN (10 mg). The tube was sealed with a septum secured with steel wire and degassed by freeze/evacuate/thaw. The polymerization mixture was allowed to stand at room temperature for seven days, during which the material solidified. It was dissolved in CH_2Cl_2 and precipitated into a 10:1 acetone/water mixture. This precipitate was filtered and dried overnight in a vacuum oven.
11. Molecular weights were measured by size exclusion chromatography (SEC) using tetrahydrofuran as the eluent and polystyrene standards for calibration.
12. Yamada, B., Satake, M. and Otsu, T., *Makromol. Chem.*, 1991, **192**, 2713.