Thermotropic aqueous gels and solutions of *N,N*-dimethylacrylamide–acrylate copolymers

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Copolymers of *N,N*-dimethylacrylamide (DMA) with C_1–C_4 alkyl and alkoxyethyl acrylates form aqueous solutions with lower critical solution temperatures (*LCST*) between 0 and 100°C. As weakly crosslinked gels they exhibit strong cloud points and volume shrinkage with rising temperature. Copolymers of DMA with higher alkyl acrylates are insoluble down to 0°C, but form hydroplastics and hydrogels with strong cloud points. The *LCST* is determined by the hydrophobicity and amount of comonomers. The ability of these copolymers to form aqueous solutions with *LCST*s can be attributed to a random copolymer structure, which allows an abrupt phase transition from a fully hydrated to a predominantly hydrophobically interacting polymer.

(Keywords: lower critical solution temperature; thermotropic hydrogels; *N,N*-dimethylacrylamide)

INTRODUCTION

The solubility of a polymer in a solvent is determined by the balance of polymer–polymer and polymer–solvent interactions. When a polymer contains groups with very different chemical affinities, for instance polar hydrophilic and non-polar hydrophobic groups, each group contributes independently to solubility. Polymers with such dual affinity can be completely soluble in water, if water is such a good solvent for the hydrophilic part of the mer unit, that any neighbouring hydrophobic part is also completely hydrated. However, when the temperature of the polymer solution is increased, hydrogen bonds are weakened and hydration is reduced; as the previously suppressed hydrophobic group interactions grow, solvated hydrophobic groups lose their weakly bound water until they coalesce into a water-insoluble, separate phase and the polymer precipitates. This temperature is called a lower critical solution temperature (*LCST*).

In hydrophilic–hydrophobic polymers in which water solubility depends on weakly hydrogen-bonding ether or amide groups, that transition from a fully hydrated and soluble polymer to a phase-separated, insoluble polymer can occur at relatively low temperatures. Many poly(ethylene oxide) based surfactants have *LCST*s above 70°C, generally referred to as cloud points. The structure of peptides and proteins too in an aqueous environment depends on a very heat-sensitive balance of hydrophilic and hydrophobic interactions; synthetic thermosensitive polyamide hydrogels with pendent α-amino-acid groups have also been described[1].

Most recent work has been carried out on poly(*N*-alkylacrylamide)s, especially poly(*N*-isopropylacrylamide) (p-NIPAM), which is one of the best studied of thermotropic, water-soluble polymers[2–6]; it has an *LCST* of approximately 32°C in aqueous solution. Reversible precipitation from solution and the reversible collapse of slightly crosslinked p-NIPAM gels at the *LCST* have been used or proposed for applications ranging from heat-activated sunscreens[7] to heat-activated drug release and absorption processes[8]. In the homologous series of poly(*N*-alkylacrylamide)s, p-NIPAM occupies a middle ground between very soluble poly(acrylamide), poly(*N*-methylacrylamide) (no *LCST* below 95°C) and poly(*N*-ethylacrylamide) (*LCST* 80°C), and much more insoluble poly(*N*-n-butylacrylamide)s (*LCST* 25°C) and higher poly(*N*-alkylacrylamide)s. Copolymers of NIPAM with more hydrophobic comonomers have a lower *LCST* and those with more hydrophilic comonomers have a higher *LCST*, as one would expect[9].

Copolymers of NIPAM and *N*-isopropylmethacrylamide with *LCST*s between 23 and 40°C have also been reported, as well as poly(*N*-n-propylacrylamide) (*LCST* 16–19°C); poly(*N*-n-propylmethacrylamide) (*LCST* 22–29°C); poly(*N*-isopropylacrylamide) (*LCST* 23°C); poly(*N*-isopropylmethacrylamide) (*LCST* 40°C); poly(*N*-ethylmethacrylamide) (*LCST* 54–57°C); poly(*N*-cyclopropylacrylamide); poly(*N*-acroylpiperidine) (*LCST* 4–6°C); poly(*N*-methacroylpiperidine) (*LCST* 18–42°C); poly(*N*-pyrrolidylmethylacrylamide) (*LCST* 53°C); and poly(*N*-piperidylmethylacrylamide) (*LCST* 42°C)[10]. Poly(*N,N*-diethylacrylamide) is the only *N,N*-dialkyl derivative with a reported *LCST* of 30–32°C[11,12].

Rather than controlling the *LCST* of poly(acrylamide)s by synthesis and polymerization of specific monomers, we investigated the more practical copolymerization approach using readily available monomers: *N,N*-dimethylacrylamide (DMA) for the weakly hydrogen-bonding amide component and alkyl acrylates as comonomers with a wide range of hydrophobic groups. While DMA forms a completely water-soluble homopolymer and the poly(alkyl acrylate)s are all water-insoluble, their random copolymers carry hydrophilic

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and hydrophobic groups in close proximity and should therefore, in an aqueous environment, behave similarly to poly(*N*-alkylacrylamide)s.

EXPERIMENTAL

Materials, synthesis and test methods

Most monomers were freshly distilled before use; *N*-isopropylacrylamide, decyl-, dodecyl- and octadecyl-acrylate were used as received from Aldrich Chemical Corporation. Linear polymers were synthesized in 50% ethanol, using 0.2% 2,2′-azobis(2,4-dimethylpentanenitrile) (VAZO-52) as initiator and stirring the reaction mixture at 50°C for 24 h under a nitrogen blanket, followed by addition of a second charge of 0.1% VAZO-52 and another 24 h reaction time at 50°C; the polymers were isolated by drying at 70°C in high vacuum to constant weight. Conversion to polymer was generally greater than 98%.

To determine copolymerization behaviour, copolymerizations of various monomer mixtures were interrupted at total conversions of ~5%. The polymers were isolated by precipitation in heptane, washed with heptane, dried, and their composition determined by elemental analysis via combustion techniques (C/H/N analyser from Control Equipment Corp., model 240XA; F absorbed as fluoride in water and measured with a F^- specific electrode).

Molecular weights were determined by gel permeation chromatography on a Waters-Millipore instrument, using five microstyragel columns (10^4, 10^3, 2 × 500 and 100 Å), 100 ml of 1% solutions in tetrahydrofuran, ambient temperatures, a flow rate of 1.4 ml min^{-1} and refractive index for detection. M_n and M_w were calculated with a precision of ±10% and are based on polystyrene standards; the values are therefore only relative, not absolute.

For the synthesis of crosslinked polymers X1–X16, 0.2% Daracure-1173 (a u.v. initiator from EM Chemicals) was added to the monomer mixture, which was degassed and sparged with dry nitrogen and transferred into a flat mould consisting of 10.2 cm × 10.2 cm glass plates lined with clear Mylar and held together by clamps, using 0.5 mm silicone cord as spacer. The moulds were exposed for 3 h to u.v. light from two 15 W Sylvania Blacklight Blue fluorescent lamps, 5 cm distant; then the polymer sheet was removed and equilibrated in water for 1 week.

The polymer gels were synthesized by the same procedure, but as 50% ethanol swollen gels with 1% ethylene glycol dimethacrylate as crosslinking agent.

Water contents were determined gravimetrically. Cloud points of gels and *LCST*s of 1% aqueous solutions were determined visually by immersing the samples in a water bath, whose temperature was raised at a rate of ~1°C min^{-1}. Water content is defined as:

$$\%H_2O = \frac{\text{weight of wet sample} - \text{weight of dry sample}}{\text{weight of wet sample}} \times 100$$

and swelling ratio (*SR*) as:

$$SR = \frac{\text{weight of swollen sample}}{\text{weight of dry sample}}$$

RESULTS AND DISCUSSION

Linear polymers

The number average molecular weights, M_n, of the alkyl acrylate copolymers L1–L18 (*Table 1*) ranged from 1.4×10^4 to 1.8×10^4 (1.62 average); the weight average molecular weights, M_w, ranged from 4.8×10^4 to 6.6×10^4 (5.92 average) and dispersities were accordingly high, ranging from 2.9 to 4.2 (3.67 average). For the alkoxyethyl acrylate copolymers L29–L34 (*Table 3*) the corresponding values were $M_n = 1.4 \times 10^4$–4.0×10^4 (2.2 average), $M_w = 5.3 \times 10^4$–12.4×10^4 (8.1 average) and dispersities ranged from 2.3 to 5.3 (3.9 average).

Polymers with an LCST. *Tables 1*, *2* and *3* and *Figure 1* show the *LCST*s of DMA copolymers with varying

Table 1 *LCST*s of 1% aqueous *N*,*N*-dimethylacrylamide/C_1–C_4-n-alkyl acrylates copolymer solutions

	Alkyl acrylate comonomer				
Copolymer	Alkyl-	(wt%)	(mol%)	*HI*	*LCST* (°C)
L1	Methyl-	30	33	0.33	98
L2	Methyl-	40	43	0.43	65
L3	Methyl-	50	54	0.54	41
L4	Methyl-	55	59	0.59	21
L5	Methyl-	60	64	0.64	6
L6	Methyl-	70	73	0.73	<0
L7	Ethyl-	25	25	0.40	74
L8	Ethyl-	30	30	0.49	61
L9	Ethyl-	50	50	0.81	14
L10	Ethyl-	55	55	0.89	<0
L11	Propyl-	20	18	0.40	80
L12	Propyl-	30	27	0.60	44
L13	Propyl-	40	37	0.83	21
L14	Propyl-	50	47	1.05	8
L15	Butyl-	15	12	0.34	73
L16	Butyl-	20	16	0.46	50
L17	Butyl-	30	25	0.72	21
L18	Butyl-	35	30	0.86	8

Table 2 *LCST*s of 1% aqueous *N*,*N*-dimethylacrylamide/alkyl acrylate ter-copolymer solutions

	Alkyl acrylate comonomers				
Copolymer	Alkyl-	(wt%)	(mol%)	*HI*	*LCST* (°C)
L19	Ethyl-	15	14	0.62	30
	+methyl-	35	39		
L20	Ethyl-	25	24	0.66	24
	+methyl-	25	28		
L21	Ethyl-	33	32	0.71	18
	+methyl-	17	19		
L22	Ethyl-	27.5	26	0.73	13
	+methyl-	27.5	31		
L23	Ethyl-	30	29	0.78	2
	+methyl	30	33		
L24	Propyl-	25	22	0.78	19
	+methyl-	25	29		
L25	Propyl-	35	32	0.89	12
	+methyl-	15	17		
L26	Ethyl- +	45	46	0.90	7
	2-ethylhexyl-	5	2.8		
L27	Ethyl- +	40	42	1.00	3
	2-ethylhexyl-	10	5.6		
L28	Methyl- +	35	41	0.89	1
	2-ethylhexyl-	15	8.3		

Table 3 *LCSTs* of *N,N*-dimethylacrylamide/alkoxyalkyl acrylate copolymers. In this case a hydrophobicity index *HI** is calculated as the ratio of carbon/oxygen atoms in the alkoxyalkyl group × weight fraction of comonomer

Copolymer	Composition (wt%) DMA	Acrylate comonomers (B)		Mole ratio DMA/B	*HI**	*LCST* (°C)
L29	20	Methoxyethyl-	80	0.41	2.4	30
L30	25	Methoxyethyl-	75	0.44	2.25	36
L31	30	Methoxyethyl-	70	0.56	2.1	45
L32	50	Methoxyethyl-	50	1.32	1.5	75
L33	25	Ethoxyethyl-	75	0.48	3.0	12
L34	50	Ethoxyethyl-	50	1.43	2.0	46
L35	50	$(Ethoxy)_2$ethyl-	50	1.89	1.5	62
L36	50	n-Butoxyethyl-	50	1.68	3.0	<0

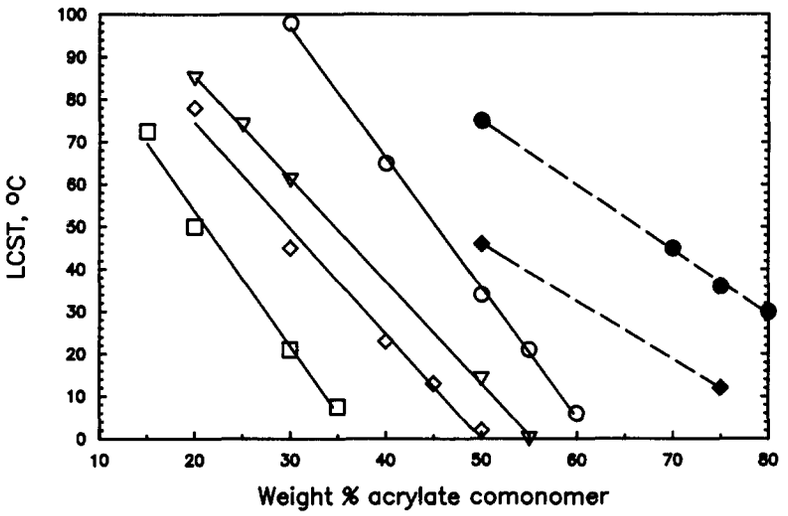

Figure 1 *LCST* of DMA/n-alkyl acrylate and alkoxyalkyl acrylate copolymer solutions (1%) as a function of weight per cent comonomer and alkyl or alkoxyalkyl chain length. Comonomer acrylate: ○, methyl-; ▽, ethyl-; ◇, n-propyl-; □, butyl-; ●, methoxyethyl-; ◆, ethoxyethyl-

amounts of lower alkyl and alkoxyethyl acrylates; the *LCST* decreases in a predictable fashion with an increase in comonomer content and increasing chain length, that is hydrophobicity, of the alkyl or alkoxyethyl group, with the latter being more hydrophilic. The hydrophobicity of a copolymer is in rough approximation an additive property of its hydrophobic groups. By assigning a value of 1 to the methyl group, one can calculate a relative hydrophobicity index (*HI*) based on the additive properties of group contributions to hydrophobic interactions: $-CH_3 = 1$; $-CH_2- = 0.62$; $-CHCH_3- = 1.14$; $-C(CH_3)_2- = 1.56$ and 3.95 for a cyclohexyl group[13]. For n-alkyl acrylate copolymers, for example, the following formula was used:

$$HI = (1 + 0.62n)f_M$$

where f_M is the mole fraction of the $CH_3(CH_2)_n$–acrylate comonomer in the polymer. This formula allows one to compare not only copolymers, but terpolymers as well and to make rough predictions of water solubility and *LCST* for polymers with other compositions; polymers with $HI < 0.4$ approach complete solubility (*LCST* → 100°C) and those with $HI > 1$, complete insolubility (*LCST* → 0°C) (*Figure 2*).

For low *HI* values, between 0.3 and 0.7, the *LCST–HI* relationship is steep and quite linear; for methyl acrylate copolymers the relationship is linear over the whole temperature range. A line drawn through all data for 70 wt% DMA copolymers is straight (*Figure 2*, insert), indicating that the *HI*, as calculated, is indeed a fairly realistic measure of hydrophobicity, at least for the n-acrylate copolymer series.

At the higher *HI* values of polymers with low DMA content and of copolymers with higher alkyl acrylates, the *LCST/HI* slope decreases. The explanation lies in the stoichiometry of the polymer. Only in polymers with high DMA content can the incremental hydrophobic interaction of each additional methyl or methylene group have a maximal effect on their hydration by neighbouring water-bonding amide group. In polymers with low DMA content with fewer neighbouring amide groups, only part of the additional hydrophobic interaction can have that effect and hydrophilicity is increasingly determined by hydration of DMA alone.

A similar relationship exists between the *LCSTs* of the DMA/alkoxyethyl acrylate copolymers and the hydrophobicity of the alkoxyethyl group; here the ratio of carbon/oxygen atoms in the alkoxyethyl group was taken as a relative measure of hydrophobicity (*Table 3*).

Hydroplastics. Above their *LCST* the polymer solutions coalesce into water-plasticized masses, ranging

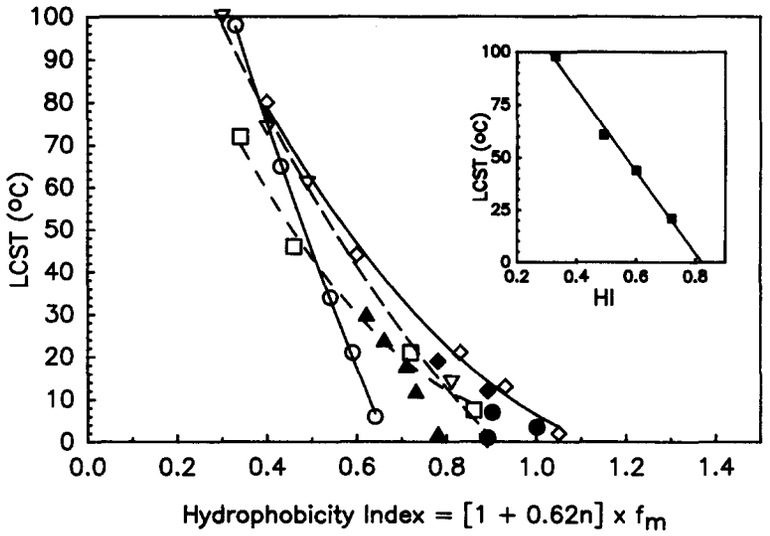

Figure 2 *LCSTs* of DMA/$CH_3(CH_2)_n$-acrylate copolymer solutions (1%) as a function of their hydrophobicity index. Acrylate comonomers: ○, methyl; ▽, ethyl; ◇, n-propyl; □, n-butyl; ●, 2-ethylhexyl + methyl/ethyl; ▲, methyl + ethyl; ◆, methyl + propyl (from *Tables 1* and *2*). Insert graph shows *LCSTs* of 30% comonomer compositions (methyl-, ethyl, n-propyl- and n-butyl acrylate)

Table 4 Hydroplastic DMA–alkyl acrylate copolymers, containing 50 wt% DMA

Copolymer	Alkyl acrylate comonomer (A)		Mole ratio DMA/A	*HI*	Water content at 25°C (%)
	Alkyl-	(mol%)			
L9	Ethyl-	50	1.0	0.81	82
L14	n-Propyl-	47	1.1	1.05	75
L37	t-Butyl-	44	1.3	1.13	54
L38	Isobutyl-	44	1.3	1.21	44
L39	n-Butyl-	44	1.3	1.26	41
L40	n-Heptyl-	37	1.7	1.75	40
L41	n-Octyl-	35	1.9	1.87	42
L42	2-Ethylhexyl-	35	1.9	1.83	39
L43	n-Decyl-	32	2.1	2.11	41
L44	n-Dodecyl-	30	2.3	2.05	43

from free-flowing, high-water-content (>70%) liquids to an almost solid, tar-like consistency with water content of 40–50% (for 50 wt% DMA copolymers). As water-insoluble, but highly water-swollen viscous polymer liquids, they can appropriately be called hydroplastics, as opposed to hydrogels, their crosslinked, non-flowing equivalents. Linear polymers with $HI > 1$ are hydroplastic down to 0°C; their hypothetical transition temperature (*LCST*) is below 0°C.

In copolymers with higher than C_4-alkyl acrylates the water content is only slightly influenced by the nature of the comonomer; for polymers containing 50 wt% DMA the water content levels out at ~42% (*Table 4*). Even above the *LCST*, the water content of the hydroplastic drops slowly with rising temperature, an effect more easily investigated on slightly crosslinked gels.

Crosslinked gels

Weakly crosslinked aqueous gels of DMA–acrylate copolymers (*Tables 5* and *6*) behave much like their non-crosslinked analogues, except that any *LCST* is replaced by a large volume contraction (*Figures 3* and *4*), expressed here as changes in swelling ratio; the swelling ratio (*SR*) as defined, is a good measure for large weight or volume changes, but the accompanying changes in water content ($\%H_2O = 10 - 100/SR$) may be very small; a 50% drop in volume from $SR = 25$ to 12.5 corresponds to a drop in $\%H_2O$ from 96 to 92%.

Strong temperature-dependent volume change, indicative of a true phase transition, is observed only with the most hydrophilic gels, in which the comonomer is either an acrylate or acrylate mixture with an average of no more than three carbon atoms in the alkyl group and $HI < 1$ (*Figures 3* and *5*), or where the comonomer is methoxy- and ethoxyethyl acrylate (*Figure 6*). Between 0°C and their transition point those polymers are thermodynamically close to dissolution, held together only by their crosslinks.

The degree of temperature-induced gel shrinkage for the most hydrophilic DMA–acrylate copolymer gels is comparable to that of a p-NIPAM gel synthesized by the same procedure (*Figure 5*). (A p-NIPAM gel swelling minimum similar to that in *Figure 5* is also reported in the literature[14].) Higher degrees of gel contraction are a

Table 5 Cloud points of crosslinked DMA/alkyl acrylate copolymers (w = weak, vw = very weak, st = strong). See *Figures 3* and *7* for volume shrinkage

Copolymer	Composition[a] Acrylate (A)	(mol%)	Mole ratio DMA/A	*HI*	Cloud point effect	*LCST* of linear polymer (°C)
X1	Methyl-	54	0.87	0.54	w	41
X2	Ethyl-	50	1.00	0.81	st	14
X3	n-Propyl-	47	1.15	1.05	st	8
X4	t-Butyl-	44	1.29	1.13	st	<0; HP[b]
X5	Isobutyl-	44	1.29	1.21	st	<0; HP[b]
X6	n-Butyl-	44	1.29	1.26	st	<0; HP[b]
X7	Cyctohexyl-	38	1.58	1.50	st	<0; HP[b]
X8	Octyl-	34	1.86	1.87	st	<0; HP[b]
X9	2-Ethylhexyl-	34	1.86	1.83	st	<0; HP[b]
X10	Decyl-	31	2.00	2.11	st	<0; HP[b]
X11	Dodecyl-	28	2.28	2.05	w	<0; HP[b]
X12	Octadecyl-	23	3.13	2.65	vw	<0; HP[b]
X13	C_6F_{13}Ethyl-	19	4.22	–	none	<0; HP[b]

[a]50% DMA, 0.1% ethylene glycol dimethacrylate
[b]Hydroplastic behaviour of non-crosslinked polymer analogues

Table 6 Water contents at 20°C of DMA–methyl/ethyl acrylate (1:1 weight ratio) ter-copolymer hydrogels; bulk synthesis. See *Figure 4* for gel shrinkage

Copolymer	Composition[a] DMA (%)	Methyl/ethyl-A (mol%)	Mole ratio DMA/A	*HI*	*LCST* of linear polymer (°C)
X14	50	28/24	0.92	0.66	24
X15	45	31/26	0.75	0.73	13
X16	40	33/28	0.64	0.78	2
X17	30	39/33	0.39	0.92	<0

[a]0.1% ethylene glycol dimethacrylate; A = acrylate

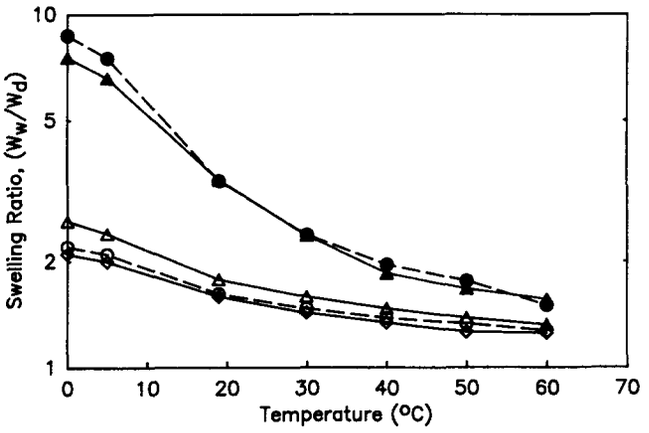

Figure 3 Swelling ratio as a function of temperature for 50 wt% DMA/50% ethyl-, propyl- and butyl-acrylate copolymer hydrogels; bulk synthesis with 0.1% ethylene glycol dimethacrylate as crosslinking agent. Acrylate comonomer: ●, ethyl-; ▲, propyl-; △, t-butyl-; ○, isobutyl-; ◇, n-butyl-

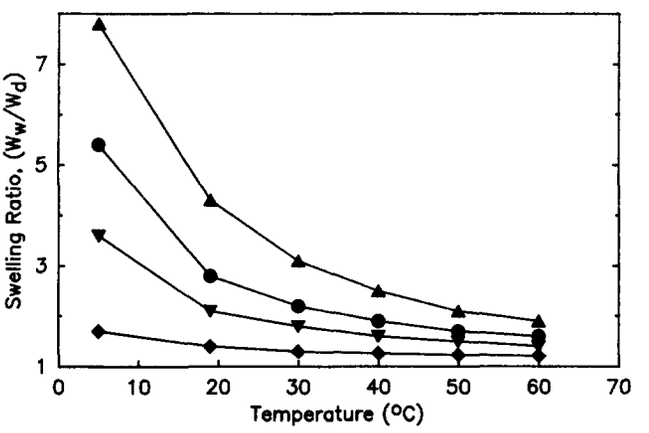

Figure 4 Swelling ratio as a function of temperature for DMA/ethyl-, methyl acrylate (1:1 by weight) copolymer hydrogels; bulk synthesis with 0.1% ethylene glycol dimethacrylate as crosslinking agent (see *Table 6*). DMA content (wt%): ▲, 50; ●, 45; ▼, 40; ◆, 30

result of even higher initial swelling ratios, that is very low crosslink densities; as such they are extremely dependent on synthesis conditions, for instance the presence of diluting solvents and monomer conversion[15]. Gels below their hypothetical *LCST* have a homogeneous hydrophilic, very open matrix, whereas above this transition temperature the matrix is separated into much denser hydrophobic and hydrophilic domains. Above the *LCST*, or the temperature range of strong gel contraction, temperature-dependent volume change

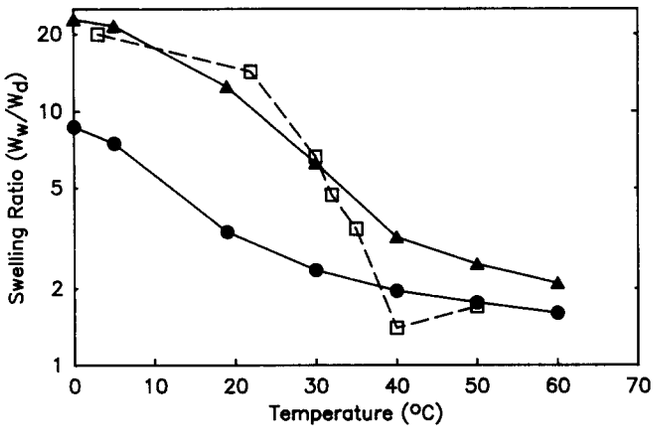

Figure 5 Swelling ratio as a function of temperature for 50 wt% DMA/50% ethyl acrylate (●) and methyl/ethyl acrylate (▲) copolymer hydrogels and p-NIPAM (□) hydrogel; synthesis carried out in 50% ethanol with 1% ethylene glycol dimethacrylate as crosslinking agent

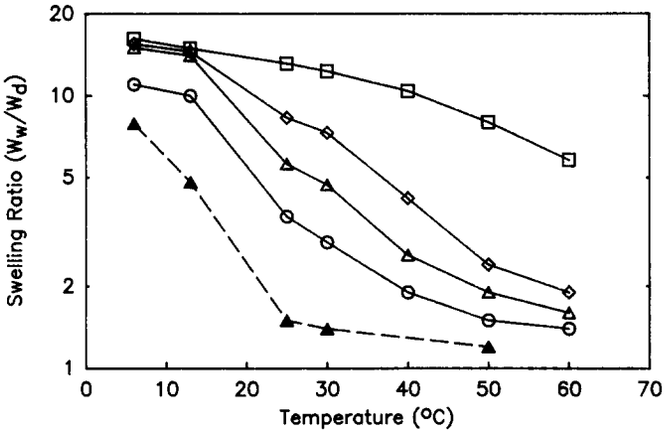

Figure 6 Swelling ratio as a function of temperature for DMA/methoxyethyl acrylate (MOEA) and ethoxyethyl acrylate (EOEA) copolymer hydrogels; bulk synthesis with 0.1% ethylene glycol dimethacrylate as crosslinking agent (see also *Table 3*). Comonomer content: ○, 80% MOEA; △, 75% MOEA; ◇, 70% MOEA; □, 50% MOEA; ▲, 75% EOEA

gradually becomes smaller, as is typical for gels whose corresponding linear counterparts would be too hydrophobic to show an *LCST* at all, namely those made with low DMA content, or with higher than C_3-alkyl acrylates (*Figures 3*, *4* and *7*).

After the weakly bound water which surrounds and hydrates the hydrophobic mer units is quickly lost during gel collapse, the remaining water hydrating the DMA units is lost more gradually; at equal DMA/acrylate weight ratios, the rate of further water loss over a given temperature range is lower for the more hydrophobic, high M_w acrylates (*Figure 7*).

Even above their transition temperature, all gels are clear after equilibration of water, probably because in crosslinked polymers the extent of phase separation – the domain size – is limited. Because of their remaining temperature sensitivity, however, they turn opaque with a rise in temperature due to further segregation of a dispersed free water phase; unless water out-diffusion is prevented, they then slowly shrink in volume and re-equilibrate into clear gels at the higher temperature. These transient cloud points are unrelated to the *LCST*.

The higher the water loss per °C temperature rise, the faster and stronger is the opacifying effect. The strength of the effect at a given temperature can therefore be predicted from the slope of the temperature/swelling ratio plot. When warmed from room temperature, the fast opacifying gels, with strong transient cloud points between 25 and 35°C, are those containing the very hydrophobic C_4- to C_{10}-alkyl acrylates as comonomers, including cyclohexyl acrylate. The dodecyl acrylate-based gel shows a weak cloud point at 50°C and the octadecyl acrylate gel a very faint one at ~80°C. These findings are indicative of the progressively smaller degrees of temperature induced deswelling (*Figure 7*). The 1,1,2,2-tetrahydroperfluorooctyl acrylate copolymer gel shows no cloud point (*Table 5*).

In butyl acrylate copolymers hydrophilicity decreases in the order t-butyl, isobutyl to n-butyl (*Tables 4* and *5*, *Figure 3*); a similar trend (as a result of increasing hydrophobic interactions) has been reported for the series of poly(*N*-cyclo-, *N*-iso- and *N*-n-propylacrylamide)s[16].

Effect of polymer structure

The strong thermotropic behaviour of the DMA–acrylate copolymers in aqueous media is due to the close proximity of very hydrophobic groups and the hydrogen-bonding amide groups in the polymer chain; in this, they resemble p-NIPAM. In p-NIPAM the density of hydrophilic and hydrophobic groups along the polymer chain is double that of DMA–acrylate copolymers and their stoichiometric balance is perfect. DMA–acrylate copolymers are random, rather than strictly alternating in structure; they contain a distribution of different monomer sequences within their chain. Therefore, while the *LCST* and rapid gel collapse of p-NIPAM defines a sharp transition, independent of molecular weight and strictly a function of chain configuration[17], the *LCST* and wider temperature range of gel contraction of a DMA–acrylate copolymer represents a composite of the *LCST*s of the many possible chain segment compositions and chain configurations obtained by free radical random copolymerization, especially one that includes chain transfer reactions to the polymer.

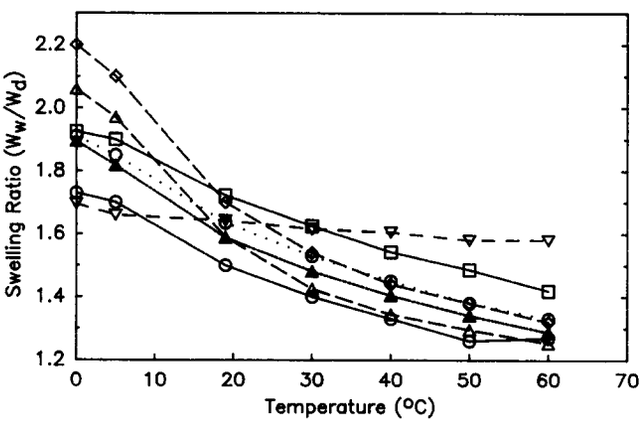

Figure 7 Swelling ratio as a function of temperature for 50 wt% DMA/50% higher-alkyl acrylate copolymer hydrogels; bulk synthesis with 0.1% ethylene glycol dimethacrylate as crosslinking agent. Acrylate comonomer: △, butyl-; ▲, octyl-; ○—, 2-ethylhexyl-; ○. . ., decyl-; □, dodecyl-; ▽, octadecyl-; ◇, cyclodecyl-

Table 7 Comparison of DMA/acrylate and DMA/methacrylate copolymer hydrogels crosslinked with 0.1% ethyleneglycol dimethacrylate

Composition (wt%)[a]			Appearance	Cloud point (°C)	Water content at 20°C (%)
DMA	Acrylate	Methacrylate			
40	EHA	–	Clear	Strong (25)	20
40	–	EHMA	Hazy	Weak (>90)	29
50	EHA	–	Clear	Strong (24)	34
50	–	EHMA	Clear	Weak (>90)	46
50	BA	–	Clear	Strong (27)	36
50	–	BMA	Clear	None	52

[a]EHA = 2-ethylhexyl acrylate; EHMA = 2-ethylhexyl methacrylate; BA = n-butyl acrylate; BMA = n-butyl methacrylate

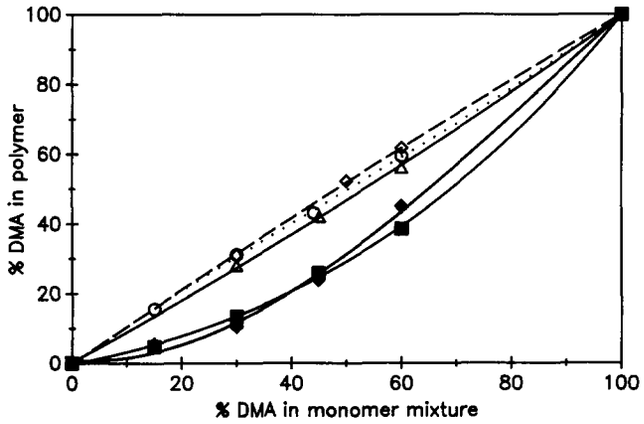

Figure 8 Copolymerization behaviour of DMA/acrylate and DMA/methacrylate comonomer systems: monomer composition *versus* polymer composition at ~5% conversion. Comonomers: ○, ethyl acrylate; ◇, 2-ethylhexyl acrylate; △, C_6F_{13}ethyl acrylate; ■, 2-ethylhexyl methacrylate; ◆, C_6F_{13}ethyl methacrylate

As the DMA/comonomer mole ratio increases, as it necessarily does with higher M_w acrylates when weight ratios are kept constant, the polymer structure becomes more and more block-like, even with random copolymerization. With an average of two or more vicinal DMA units in the polymer chain, the thermotropic effects of gel shrinkage and cloud point become very weak and at higher DMA/comonomer mole ratios they disappear altogether, even as the DMA content remains at 50 wt% (*Table 5*, *Figure 7*).

In contrast to the acrylate copolymers, the DMA–methacrylate copolymer hydrogels do not exhibit thermotropic behaviour (or exhibit it only to a much weaker degree), nor are they random copolymers (*Figure 8*). If an even distribution of hydrophobic groups provides more effective shielding of the hydrophilic groups, one would also expect a lower equilibrium water content (or swelling ratio) for the random, lower-alkyl acrylate copolymers with very short DMA sequences, than for more block-like methacrylate and higher-alkyl acrylate analogues with longer DMA sequences; this is indeed the case (*Table 7*, *Figure 7*, 60°C values).

CONCLUSION

Linear or crosslinked DMA copolymers with alkyl or alkoxyethyl acrylates constitute a new class of thermotropic hydroplastics and hydrogels which are easily prepared from commercially available monomers. Dependent on the comonomer chosen, they can exhibit *LCSTs* from 0°C to over 90°C or, as gels, show strong temperature-dependent shrinkage. They can be made in the form of opacifying sheets or as dilute aqueous solutions, but also in the form of beads swellable by water. They are of interest in a variety of applications, such as heat-activated sunscreens and valves, and in absorption and release processes.

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