Latent reactive groups unveiled through equilibrium dynamics and exemplified in crosslinking during film formation from aqueous polymer colloids†

David J. Berrisford,*[a] Peter A. Lovell,*[b] Nadia R. Suliman[ab] and Andrew Whiting*[c]

Received (in Cambridge, UK) 25th August 2005, Accepted 28th September 2005
First published as an Advance Article on the web 20th October 2005
DOI: 10.1039/b512073j

The concept of using equilibrium dynamics to provide for both protection and unveiling of latent functional groups at appropriate times in aqueous polymer colloid coatings designed for crosslinking only during film formation is introduced; the new functional monomer, 4-hydroxyethylsulfonylstyrene (HESS), readily undergoes emulsion copolymerization with acrylates to form stable latexes, followed by crosslinking by loss of water during film formation.

Release of volatile organic compounds (VOCs) into the environment is a major global issue. A significant contribution to VOC release is made by the use of solvent-borne coatings, but the move towards materials that liberate no VOCs is difficult to achieve without loss of coating performance. One issue is the need to combine stability during storage with a robust crosslinking methodology that operates only when needed.[1] The crosslinking reaction must not liberate VOCs and the level of coating performance must at least match that from traditional technologies. A large number of different chemistries have been investigated for crosslinking of water-borne coatings, but no current system satisfies all the requirements. In parallel with growth of this need, there has been increased understanding of how to engineer molecular systems, particularly macromolecules, which respond to their environment and, in doing so, trigger a chemical process.[2] A fundamental requirement for crosslinkable aqueous polymer colloid (*e.g.* latex) coatings is that they must be unreactive during storage, but reactive to crosslinking during film formation. This led us to consider a previously unexploited, general principle of using loss of water from the latex during film formation to trigger crosslinking. Thus, an ideal scenario is an equilibrium process involving water that unveils a reactive group which is then able to crosslink (Fig. 1). In principle, a dynamic equilibrium[2] is established between a functional group which is unreactive to crosslinking and a derivative that readily crosslinks by reaction with other functional groups present. Excess water in the latex will quench any reactive intermediate generated during storage, preventing premature crosslinking and so providing a built-in protective function. Loss of water during film formation, however, triggers re-establishment of the equilibrium, favoring the reactive form and leading to irreversible crosslinking.

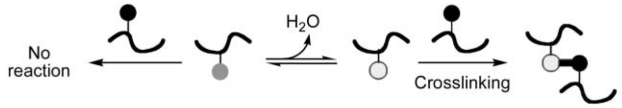
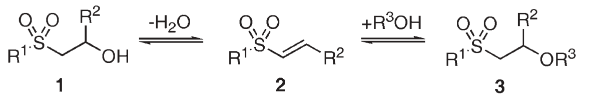


Fig. 1 Representation of the crosslinking principle with spheres representing functional groups on polymer chains. A dynamic equilibrium unveils a reactive group from a dormant group as water evaporates during film formation, resulting in reaction of mutually-reactive functional groups to give a crosslink (bold line).

To demonstrate the feasibility of this approach, we report the synthesis, polymerization and crosslinking chemistry for monomers incorporating a hydroxyethylsulfone **1** (Scheme 1), a prototypical latent reactive functional group.[3] Such hydroxyethylsulfones are in equilibrium with vinylsulfones **2** through loss of water; the equilibrium normally lying well to the left. Vinylsulfones **2** are potent Michael acceptors and readily react with heteroatomic and carbon nucleophiles (including water); such chemistry is exploited in reactive dye technology[4] and solid phase synthesis.[5] In the context of crosslinking, incorporation of nucleophilic groups for reaction with **2** can be accomplished through copolymerization with an appropriate second functional monomer. Conjugate addition affords **3**, which represents a crosslink for reactions between functional groups pendent to polymer chains. The process of converting **1** into **3** is rendered irreversible by loss of water. Furthermore, this conversion increases the local hydrophobicity, further excluding water and disfavoring hydrolysis of **3**. In contrast, when an excess of water is present, for example during latex storage, any vinylsulfone **2** that is generated should recombine with water to regenerate **1**, hence preventing premature crosslinking.

In order to investigate this principle, we examined a series of functional monomers containing acrylate, methacrylate and



Scheme 1 Equilibration of 2-hydroxyethylsulfones with vinylsulfones and the crosslinking reaction (exemplified with R^3OH).

---

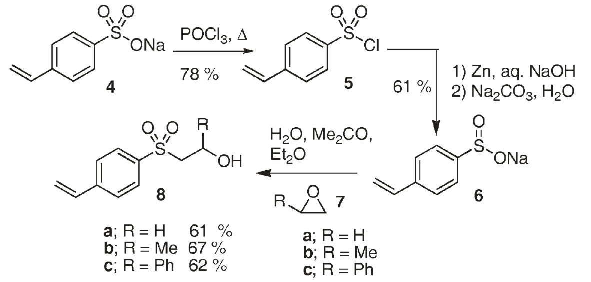
[a] *School of Chemistry, Faraday Building, University of Manchester, Sackville Street, PO Box 88, Manchester, UK M60 1QD. E-mail: david.berrisford@manchester.ac.uk*
[b] *Materials Science Centre, School of Materials, University of Manchester, Grosvenor Street, Manchester, UK M1 7HS. E-mail: peter.lovell@manchester.ac.uk*
[c] *Department of Chemistry, Durham University, Science Laboratories, South Road, Durham, UK DH1 3LE. E-mail: andy.whiting@durham.ac.uk*

† Electronic supplementary information (ESI) available: synthetic methods and characterization data for compounds **4**, **5**, **6** and **8**, the emulsion polymerization formulation and procedure, and the film formation, gel fraction measurement, and tensile testing procedures. See DOI: 10.1039/b512073j

styrene functions. However, only the styrene function was fully compatible with the chemical methods required to access such systems; the resulting synthesis is shown in Scheme 2.[6] *para*-Styrenesulfonate **4** was converted[7] to the sulfinate salt **6**[8] *via* a chlorination–zinc reduction sequence. The resulting sulfinate salt **6** undergoes facile reaction with epoxides, as outlined in Scheme 2, to yield the corresponding substituted hydroxyethylsulfones **8**.

Latexes were prepared by two-stage semi-continuous emulsion copolymerizations using n-butyl methacrylate (BMA) and n-butyl acrylate (BA) as principal monomers and **8a–c** as functional monomers. Poly(BMA) seed particles were formed first and then grown under monomer-starved conditions so that copolymer composition was controlled by feed mixture composition.[9] Each of **8a–c** satisfactorily underwent emulsion copolymerization to high conversion and gave stable latexes, but those from **8b** and **8c** failed to give significant crosslinking during film formation. However, proof of principle of our new concept for crosslinking was achieved[6] using HESS **8a** from which a series of latexes were prepared (Table 1). The growth-stage feed mixture contained HESS **8a** with an equal mol% of hydroxypropyl methacrylate (HPMA) (to introduce pendent hydroxyl groups which increase the equilibrium level of water within the particles and then react with vinylsulfone functions unveiled from HESS units during film formation), and BMA/BA (to form the main polymer backbone). For each latex containing HESS (designated R), an equivalent latex was prepared replacing HESS by styrene (designated U).

The fraction of polymer that is crosslinked (the gel fraction) in the latex form was negligible ($\ll$ 1 wt% of polymer) for all six latexes and did not change with time. Thus HESS-containing latexes are stable and do not undergo crosslinking during storage (for periods of at least 6 months). Films cast from U-coded latexes had negligible gel fractions, whereas all films from HESS-containing latexes had significant/high gel fractions (see Table 2). These observations provide unambiguous evidence that crosslinking occurs only in the presence of HESS repeat units.



Scheme 2 Synthesis of hydroxylethylsulfonylstyrenes (details are in the supplementary information; **8a** R = H is referred to as HESS).

Table 1 Comonomer compositions (mol%) used in the particle growth stages to prepare latexes for comparative tests[a]

	Latex Code[b]					
Monomer	R1	U1	R2	U2	R3	U3
BMA	90	90	80	80	68	68
BA	0	0	0	0	12	12
HESS	5	0	10	0	10	0
Styrene	0	5	0	10	0	10
HPMA	5	5	10	10	10	10

[a] The poly(BMA) core comprises 12.3 wt% of the final particle. [b] R indicates a reactive latex (prepared with HESS) and U indicates an unreactive latex (prepared with styrene replacing HESS).

Increasing the level of HESS **8a** from 5 to 10 mol% increases the gel fraction, but by less than expected based solely on composition because chain mobility also is important. Differential scanning calorimetry showed that the glass transition temperature (T_g) for the R1 copolymer is 23 °C while that of R2 is 28 °C. Crosslinking will be retarded if there is insufficient local chain motion to bring functional groups into close proximity. In accord with this hypothesis, latex R3, prepared with a small proportion of BA and having a copolymer T_g of 21 °C, gave the largest gel fraction, the corresponding control latex U3 (T_g = 22 °C) again giving no crosslinking. Two weeks after casting, the gel fraction of the film from R3 approaches the limiting value (87.7 wt% – the non-functionalized poly(BMA) phase comprises 12.3 wt%), while the other R-coded latexes crosslink much more slowly.

Tensile properties of the films were measured at 23 °C. As expected, R3 has much higher Young's modulus (336 MPa *cf.* 188 MPa) and yield stress (10.9 MPa *cf.* 7.1 MPa) but lower ultimate elongation (210% *cf.* 280%) than the corresponding control latex U3. Given the similarity in backbone structure and T_g, these data further confirm the crosslinking achieved using HESS.

Finally, there is a dramatic effect upon adjusting latex pH just prior to coating, exemplified here by experiments with latex R3. At a pH of $\leqslant$ 6.2 or $\geqslant$ 8.5, the gel fraction in the film reaches the expected value (*ca.* 80 wt%) one week after casting. However, at pH 7 no crosslinking occurs at room temperature and heating to 60 °C does not effect crosslinking. Hence, crosslinking proceeds at room temperature under mildly acidic or alkaline conditions but not under neutral conditions. These observations are consistent with the chemistry[10] outlined in Scheme 1.

In summary, the new functional monomer HESS **8a** readily copolymerizes with acrylate monomers to form stable latexes that crosslink during film formation but not during latex storage; the crosslinking is triggered by loss of water during film formation and is pH dependent. As expected, the resulting polymer films have enhanced mechanical properties. Clearly, there is great scope for altering the structure of the hydroxyethylsulfonyl monomer and for varying the complementary functional monomer.

Thus, the results presented here establish an important new principle of using equilibrium dynamics to provide for both protection and unveiling of latent functional groups at appropriate times in aqueous polymer colloids designed for crosslinking only during film formation. This should stimulate the search for other chemistries that fulfill the criteria for VOC-free polymer coatings and help advance the move to environmentally-friendly materials.

We thank the Engineering and Physical Sciences Research Council (EPSRC) in the UK for funding of this research (GR/L58507).

Table 2 Gel fractions (given as wt%) of films formed from the latexes at different times after casting (ND = not determined)

Time after film casting	R1	U1	R2	U2	R3	U3
2 weeks	10	ND	20	ND	72–75	ND
1 month	25	0	35	0	77–82	0
3 months	28	0	43	0	80–82	0

Notes and references

1 (*a*) J. P. Howard, *Chem. Ind.*, 1996, 796; (*b*) A. Guyot, F. Chu, M. Schneider, C. Graillat and T. F. McKenna, *Prog. Polym. Sci.*, 2002, **27**, 1573; (*c*) J. W. Taylor and M. A. Winnik, *JCT Res.*, 2004, **1**, 163.

2 (*a*) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2002, **41**, 898; (*b*) *e.g.* D. H. Zhao and J. S. Moore, *J. Am. Chem. Soc.*, 2002, **124**, 9996.

3 For a related use of latent functional groups see: (*a*) P. P. Matloka, J. C. Sworen, F. Zuluaga and K. B. Wagener, *Macromol. Chem. Phys.*, 2005, **206**, 218; (*b*) K. R. Brzezinska, R. Schitter and K. B. Wagener, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1544.

4 Reactive dyes involving sulfone chemistry are well known, *e.g.*: (*a*) Z. Z. Zhu, J. M. Xia and K. C. Chen, *Dyes Pigm.*, 1991, **17**, 171; (*b*) Z. Z. Zhu, J. M. Xia and K. C. Chen, *Dyes Pigm.*, 1991, **17**, 217; (*c*) M. H. Zohdy, A. M. El Naggar and W. A. Abdallah, *Polym. Degrad. Stab.*, 1997, **55**, 185; (*d*) L. M. Jiang and Z. H. Zhu, *Dyes Pigm.*, 1998, **36**, 347; (*e*) Z. H. Zhu and L. M. Jiang, *Dyes Pigm.*, 1998, **36**, 355.

5 Sulfones are used as linkers in solid phase organic synthesis, *e.g.*: (*a*) S. B. Katti, P. K. Misra, W. Haq and K. B. Mathur, *J. Chem. Soc., Chem. Commun.*, 1992, 843; (*b*) F. E. K. Kroll, R. Morphy, D. Rees and D. Gani, *Tetrahedron Lett.*, 1997, **38**, 8573; (*c*) W. S. Wade, F. Yang and T. J. Sowin, *J. Comb. Chem.*, 2000, **2**, 266; (*d*) W. C. Cheng, M. M. Olmstead and M. J. Kurth, *J. Org. Chem.*, 2001, **66**, 5528; (*e*) W. C. Cheng and M. J. Kurth, *J. Org. Chem.*, 2002, **67**, 4387; (*f*) W. C. Cheng, M. Wong, M. M. Olmstead and M. J. Kurth, *Org. Lett.*, 2002, **4**, 741; (*g*) R. V. Connors, A. J. Zhang and S. J. Shuttleworth, *Tetrahedron Lett.*, 2002, **43**, 6661; (*h*) K. H. Kong, Y. Chen, M. Xiang, W. K. Chui and Y. L. Lam, *J. Comb. Chem.*, 2004, **6**, 928.

6 D. J. Berrisford, P. A. Lovell and A. Whiting, Hydroxyethylsulfones – new functional monomers for emulsion polymerisations; UMIST: 2004, UK Patent, PCT/GB2003/005240.

7 G. K. Biswas and P. Bhattacharyya, *Synth. Commun.*, 1991, **21**, 569.

8 (*a*) H. Kamogawa, A. Kanzawa, M. Kadoya, T. Naito and M. Nanasawa, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 762; (*b*) H. Kamogawa, T. Hayashi and M. Nanasawa, *Chem. Lett.*, 1976, 419; (*c*) H. Kamogawa, H. Inoue, H. Fukuyama and M. Nanasawa, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3010.

9 P. A. Lovell, in *Emulsion Polymerization and Emulsion Polymers*; P. A. Lovell and M. S. El-Aasser, Eds.; John Wiley & Sons: Chichester, UK, 1997, p. 239.

10 (*a*) A. Khan and A. Marsh, *Synth. Commun.*, 2000, **30**, 2599; (*b*) T. Pathak, *Eur. J. Org. Chem.*, 2004, 3361.