

High molar mass polymers by cationic polymerisation in emulsion and miniemulsion†

S  verine Cauvin,^a Fran  ois Ganachaud,^{*bc} Michel Moreau^c and Patrick H  mery^c

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The generation of poly(*p*-methoxystyrene) with a molar mass of several thousand g mol⁻¹ by cationic polymerisation in emulsion, is described here for the first time. Such a striking result was achieved by carrying out the polymerisation inside monomer droplets, thus preventing fast transfer reactions with water.

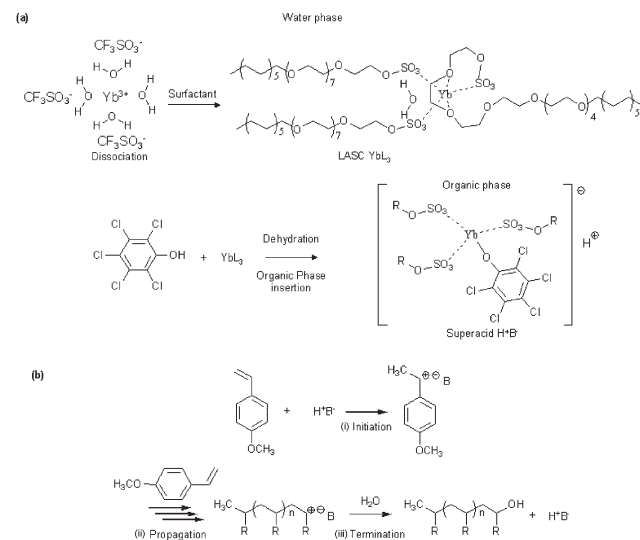
The successful cationic polymerisation of vinyl monomers in emulsions has always been a difficult (if not impossible) challenge, primarily because of transfer reactions with water. Against all expectations, polymerisation of *p*-methoxystyrene (*p*-MOS) was shown to proceed at the interface of miniemulsion droplets by using a strong acid surfactant such as dodecylbenzene sulfonic acid (DBSA).¹ Typically, protons initiate an interfacial polymerisation and generate bulky active centers that propagate rapidly. Unfortunately, the surrounding water molecules act as ‘‘chain killers’’ and stop the polymerisation at a stage when only short, non-reactive, hydroxyl-terminated oligomers have formed.‡

In recent articles, Sawamoto *et al.* have proposed the use of an initiator (either an aromatic halide² or tosylic acid³) in combination with a Lewis Acid (namely ytterbium triflate) to limit the number of growing carbocations in an attempt to regulate polymerisations. Though efficient in solution,⁴ this system produced only moderately-sized oligomers in aqueous dispersion,^{2,3} rather than polymer chains of controlled molar mass. Ytterbium triflate completely dissociates in water,⁵ and is thus inefficient as a Lewis acid. In addition, aromatic halides hydrolyse slowly, releasing HCl that promotes interfacial polymerisation.⁶ Using DBSA as the acid catalyst, an inverse (water in oil) emulsion was stabilised by the low hydrophilic–lipophilic balance (HLB) amphiphile species formed *in situ* between free ytterbium ion and the surfactant.⁷ So called Lewis Acid Surfactant Catalysts (LASC),⁸ known as efficient promoters of C–C bond formation in aqueous media, were unsuccessful at catalysing cationic polymerisation.⁶

In this communication we present a simple procedure for generating high molar mass poly(*p*-MOS) by cationic polymerisation in an emulsion. To our knowledge, this is the first report of a high molar mass polymer synthesis *via* carbocationic intermediates that takes place in the presence of excess water. To perform the synthesis, a combination of a monomer soluble LASC, **1**, and a weak organic acid (typically pentachlorophenol (PCP)) were used (Scheme 1). The LASC’s solubility in the monomer was facilitated

by the electrosteric surfactant introduced into the reaction mixture,⁵ whose constituent poly(ethylene glycol) (PEG) units wrap around the ytterbium atom and repel the ligated water. The initiator was chosen so that polymerisation was not initiated at the interface (p*K*_a = 4.5), but instead so that it associates with the LASC inside the organic phase to reversibly generate a small number of highly bulky super-acids (Scheme 1a). All polymerisation then proceeds in the bulk of the monomer droplets in three steps (Scheme 1b): (i) initiation, which is very slow due to the low quantity of super-acid generated by the unbalanced equilibrium; (ii) propagation, the fast rate of which reflects the bulkiness of the counterion (free carbocations propagate faster than ion pairs); (iii) termination by a transfer reaction with water. Contrary to previous studies where only oligomers were formed,^{1–6} here chains grew up to a molar mass of several thousand g mol⁻¹ before the few water molecules present in the hydrophobic phase transferred to the fast-propagating chains. This communication proceeds to give further details of our polymerisation procedure, its consistency and its cationic nature.

LASC **1** is a complex initially prepared *in situ* by mixing ytterbium triflate and sodium polyoxyethylene (8) lauryl sulfate in water, as traced by the decrease in turbidity of ytterbium triflate-saturated, aqueous phase and ¹H NMR measurements (Fig. S1†). The organic phase, containing the monomer and initiator, is then added to the solution of **1**. A two-phase emulsion mixture, containing a PCP upper phase with monomer droplets beneath, is



Scheme 1 (a) LASC formation in water and super-acid generation in the organic phase. (b) The cationic polymerisation mechanism proposed to take place inside the monomer droplets.

† Electronic Supplementary Information (ESI) available: Experimental, ¹H NMR spectra of surfactant and LASC **1**; particle size and size distribution changes with time; time–conversion curves; polymer/oligomer contents and total conversion with PCP concentration. See <http://www.rsc.org/suppdata/cc/b5/b501489a/>
*ganachaud@enscm.fr.

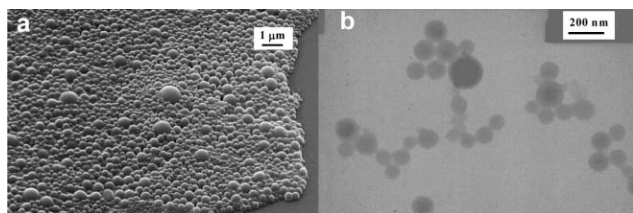


Fig. 1 (a) Scanning and (b) transmission electron microscopy photographs of a final polymer dispersion (Entry 1, Table 1).

initially produced by ultrasonication. However, the upper layer gradually disappears with time, resulting in a polymer nanodispersion with a large size distribution (Fig. S2†), observed by electron microscopy (Fig. 1). Since polymerisation proceeds in the bulk of the monomer, it would be preferable to generate stable droplets from the start. Attempts to prepare stable miniemulsions, either by adding a small quantity of a preformed poly(*p*-MOS) (not shown), or by diluting the formulation (*vide infra*) were both successful.

The kinetics were followed using a model experiment (Entry 1, Table 1). Both oligomers and polymers, whose molar masses varied with the initiator content, were produced using a variety of timescales (Fig. 2). At the beginning of the reaction only oligomers were formed by interfacial polymerisation, typical of previously reported systems^{1–6} (the natural pH of such a miniemulsion is 2). Only after an inhibition period of approximately 100 h was high molar mass polymer observed. This period relates to the slow building-up of a fine emulsion (*vide infra*). Polymerisation then proceeded slowly inside the monomer droplets, and no variation in molar masses could be observed with time (Fig. 2). This result indicates that initiation is the limiting step of the reaction. Once initiated, each chain propagates then terminates very rapidly—in other words, the polymerisation is not controlled.

Blank experiments were performed to confirm the role of each reagent. Experiments carried out in the absence of initiator PCP (average of 10 runs, Entry 2, Table 1) systematically produced very high molar mass poly(*p*-MOS) ($\approx 10^6$ g mol⁻¹). The time of polymerisation was irregular, leading us to suspect that

Table 1 Summary of main results (see ESI for experimental details)

Entry	[Initiator]/ M	MC (%) ^a	PC (%) ^a	M_n^b/\times 10^3 g mol ⁻¹	M_w^c/M_n	R (wt% h ⁻¹) ^a
1 ^b	0.03	83	76	43.2	3.0	0.73
2 ^b	/	≈ 90	≈ 90	$>10^4$	>4	— ^h
3 ^{b,d}	0.07	95	0 ⁱ	/	/	/
4 ^{b,e}	0.07	75	58	21.1	2.7	0.64
5 ^b	0.04	73	59	26.9	2.3	0.52
6 ^b	0.06	60	45	23.4	2.7	0.96
7 ^b	0.07	66	41	25.1	1.9	0.52
8 ^b	0.11	72	38	11.4	1.9	0.56
9 ^b	0.21	73	9	7	3	/
10 ^c	0.02	67	43	39.4	3.8	0.33
11 ^c	0.03	66	41	38	3.6	0.33
12 ^c	0.04	65	36	25.6	2.7	0.27
13 ^c	0.07	60	36	16.8	2.6	0.26
14 ^{b,f}	0.02	38	0 ⁱ	/	/	/
15 ^{b,g}	0.02	62	47	22.0	2.2	0.10

^a MC: monomer conversion, PC: polymer content, R: polymerisation rate. ^b Concentrated conditions. ^c Diluted conditions. ^d [Yb(OTf)₃] = 0 M. ^e [YbCl₃] = 0.21 M. ^f Initiator: benzoic acid. ^g Initiator: *o*-hydroxy-acetophenone. ^h Non-reproducible results. ⁱ Only oligomers were formed.

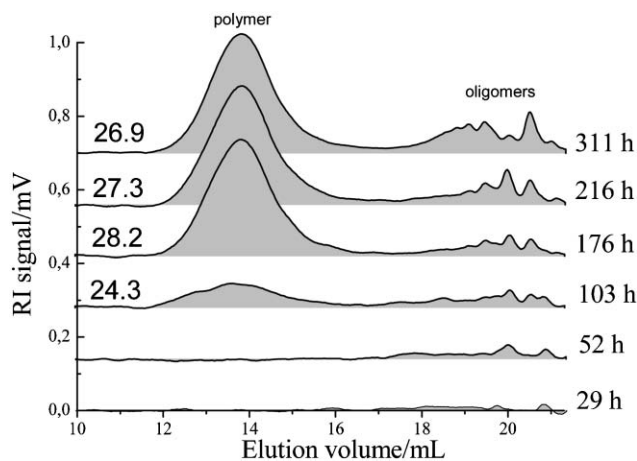


Fig. 2 Size exclusion (SEC) chromatograms recorded at different reaction times (Entry 1, Table 1). Average molar masses for polymers are given in $\times 10^3$ g mol⁻¹. Chromatograms were normalized according to the reaction conversion (monomer peak not shown).

non-reproducible thermal radical polymerisation occurred. By omitting Yb(OTf)₃ (Entry 3, Table 1) only oligomers were obtained—since ytterbium ions were not available to form the LASC. On the other hand, substituting Yb(OTf)₃ with YbCl₃ (Entry 4, Table 1) affected neither the polymerisation rate nor the molar mass, since both salts dissociate in water to release ytterbium ions (Scheme 1a). All of these results show that a combination of PCP and LASC are necessary to promote polymerisation.

The cationic nature of the polymerisation was firmly established by characterising a sample of poly(*p*-MOS) using MALDI-TOF mass spectroscopy and ¹³C NMR spectroscopy. This sample was prepared by precipitation from methanol so small oligomers were discarded. Chains with a molar mass of less than 10 000 g mol⁻¹ could only be observed by mass spectroscopy (Fig. 3a). From the results of mass calculations, we conclude that all chains are initiated by a proton originating from the super-acid, and terminated by an -OH group from a transfer reaction with water. We also compared the ¹³C NMR spectra's microstructure with those of poly(*p*-MOS) samples of similar molar masses, but prepared by conventional solution cationic polymerisation and free radical bulk polymerisation (see ESI for synthetic procedures†) (Fig. 3b). In particular, we examined the triads of the aromatic quaternary carbon C₁ (labelled * in Fig. 3a). The low resolution ¹³C NMR technique used here did not allow the clear separation of the *mr* and *rr* triads, since the 1–2–1 integration expected for the free radical sample was not resolved. However, it is striking that the poly(*p*-MOS) samples prepared in the present study and by the conventional cationic polymerisation method present similar spectra, and that both differ from the spectrum of the sample generated by the free radical route. In particular, the *mm* triad is much less prominent and the profile of the *rr* triad at 137.8 ppm is sharper and larger than for the free radical sample.§

Different reaction conditions were tested to confirm the robustness of the process. Long inhibition periods were always observed under “concentrated” conditions, irrespective of PCP concentration (Entries 1 and 4–9, Table 1. See ESI for experimental procedures†). With significant dilution of the emulsions (Entries 10–13, Table 1) the inhibition period was

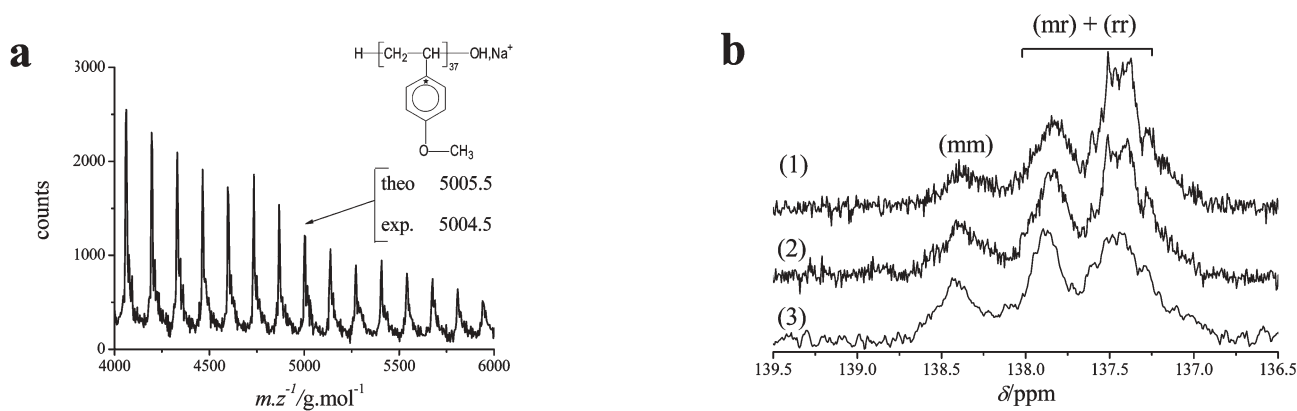


Fig. 3 (a) MALDI-TOF analysis of a precipitated poly(*p*-MOS) sample from Entry 1, Table 1 (top SEC trace in Fig. 2). (b) ^{13}C NMR spectra of poly(*p*-MOS) obtained by: (1) conventional cationic polymerisation, (2) emulsion (sample from Entry 1, Table 1) and (3) radical polymerisation.

reduced. This occurred because in these lower salt concentrations it was possible to prepare a miniemulsion made of stable, fine monomer droplets. Conversely, under the same conditions, polymerisation times were longer and molar masses reduced due to the increased swelling with water of monomer droplets (Fig. S3[†]). Conversions of monomer were systematically limited to less than 80%, most likely due to particles starting to destabilize by coagulation and coalescence. Molar masses decreased with increasing concentrations of polar initiator. Such variations are ascribed to an increase in particle water concentration rather than any application of control over the polymerisation. Besides, the proportion of oligomer (from interfacial polymerisation) to polymer (from intraparticle polymerisation) increased with PCP concentration (Fig. S4[†]), particularly in diluted conditions, and the polymer mass distributions slightly broadened. Finally, the nature of the initiator was found to be the most crucial. An initiator such as benzoic acid preferentially partitions with water, meaning only interfacial polymerisation occurs (Entry 14, Table 1). On the other hand, polymerisations carried out using an organic acid of high $\text{p}K_{\text{a}}$ (e.g. hydroxyacetophenone: $\text{p}K_{\text{a}} = 10.7$) were considerably slowed (Entry 15, Table 1).[¶]

In conclusion, high molar mass polymers can only be obtained by cationic polymerisation in aqueous dispersion if interfacial polymerisation is avoided and the chosen super-acid partitions preferentially with the monomer phase, *i.e.* the phase where all steps of the polymerisation mechanism take place. Our current work focuses on controlling the cationic polymerisation of styrene and its derivatives in miniemulsion by using much smaller quantities of new, water-tolerant Lewis acids.

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S  verine Cauvin,^a Fran  ois Ganachaud,^{*bc} Michel Moreau^c and Patrick H  mery^c

^aLaboratory of Polymer Chemistry and Technology, Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL

^bLaboratoire de Chimie Macromol  culaire UMR5076, ENSCM, 8 rue de l'  cole normale, 34296, Montpellier Cedex 5, France.

E-mail: ganachau@enscm.fr.; Fax: 33 4 67 14 72 20; Tel: 33 4 67 14 72 96
^cLaboratoire de Chimie des Polym  res UMR7610, UPMC, T44 E1 4 place Jussieu, 75252, Paris Cedex 5, France

Notes and references

[‡] Even when termination does not proceed readily, the growing oligomers become so hydrophobic that they enter the particle and stop propagating. This molar mass limit is characteristic of Ionic Polymerisation in Emulsion processes (IPE) and has been related to a "critical DP" concept (see for instance ref. 10).

[§] The inhibitors naturally present in the monomers were not removed and all experiments carried out in air. Furthermore, both ytterbium and PCP are known inhibitors of radical polymerisation, particularly in emulsions.⁹ A variety of cationic and radical inhibitors were tested to attempt to further validate the proposed mechanism of polymerisation, unfortunately without success. Amongst these, sodium hydroxide converted the LASC into a precipitate of inactive ytterbium oxide, alcohols destabilised the emulsion prematurely and amines deactivated the ytterbium by complexation to it. TEMPO (a nitroxide inhibitor) also formed an inactive blue complex with ytterbium, whereas *tert*-butyl catechol acted as a poor initiator of cationic polymerisation. Finally, styrene did not polymerise under these conditions and vinyl ethers readily hydrolysed at the emulsion's pH.

[¶] Results were also gathered under various other experimental conditions, but showed no clear trends. Increasing the temperature to 80   C favored the exclusive formation of oligomers, whereas at 40   C, polymerisation proceeded only after 3 months. Other example surfactants including anionic (sodium dodecyl sulfate and DBSA), cationic (cetyltrimethyl ammonium bromide) and non ionic (polyoxyethylene (8) lauryl ether) were not able to stabilise the emulsions at such high ionic strengths (see ref. 5)

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