Polymethylmethacrylate End-group Analysis by Matrix-assisted Laser Desorption Ionisation Time-of-flight Mass Spectrometry (MALDI-TOF-MS)

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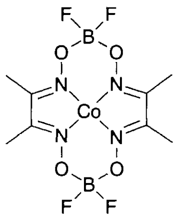
End-groups of polymethylmethacrylate from screened anionic polymerisation, catalytic chain transfer polymerisation and group transfer polymerisation are determined by matrix-assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS).

Polymer end-groups play a significant role in determining polymer properties, which becomes of increasing importance as polymer molecular weight decreases. The use of living polymerisation methodology with controlled termination allows the introduction of a range of functionality at the terminating end of the polymer molecules.[1] Similarly, functionality can also be introduced at the initiating end of the polymer by judicious choice of initiator or protected functional group initiator. Although methods to introduce functionality are well established, precise characterisation of each molecular species is not possible by traditional techniques. Bulk functionality is determined by NMR, UV–VIS, titration, *etc.*, which can be combined with molecular weight data, usually from gel permeation chromatography (GPC) to give a measure of functionality. Investigation of individual molecular species is not possible by usual chromatographic separation for all but the lowest molecular weight, $<$ *ca.* 1000 amu. Determination of the polymer end-group also gives a unique probe of the polymerisation mechanism.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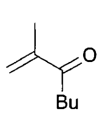
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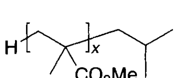
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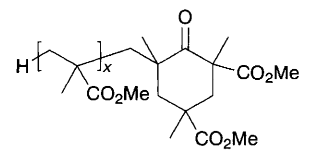
2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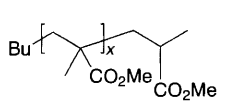
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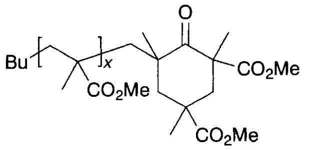
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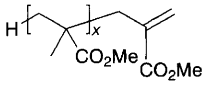
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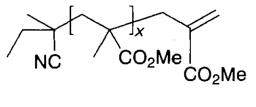
M = x(100.1) + 4
7

Mass spectrometric analysis of polymers is becoming of increasing importance.[2] A variety of soft ionisation techniques including laser desorption,[3] fast atom bombardment[4] and field desorption[5] have been used. Of particular interest is time-of-flight secondary-ion-mass spectrometry (TOF-SIMS), which has been used very effectively to give accurate end-group information for a range of polymer types. However, TOF-SIMS is somewhat restricted in molecular weight capability, usually being very effective below *ca.* 2000 amu, depending on polymer type.[6,7] MALDI-TOF-MS has been previously demonstrated to be applicable to a wide range of polymer types with reasonable resolution up to very high molecular weights, from a simple experiment.[8] Here we report the use of MALDI-TOF-MS for the mass and end-group determination of poly(methylmethacrylate) (PMMA) synthesised by three different initiating systems; screened anionic polymerisation (SAP), group transfer polymerisation (GTP) and catalytic chain transfer polymerisation (CCTP).[9,10]

PMMA of molecular mass *ca.* 2000–6000 amu (Table 1) was prepared by different polymerisation mechanisms: GTP utilised methyl trimethylsilyldimethylketeneacetal (MTS) initiator in conjunction with tetrabutyl ammonium acetate catalyst (250 : 1) in THF at 0 °C; SAP was carried out in toluene with *tert*-butyl lithium and triisobutyl aluminium initiator at 0 °C; and (CCTP) in butanone solution with 2,2′-azobis(2-methylbutyronitrile) (AMBN) and **1** as catalytic chain transfer agent at 60 °C. MALDI-TOF was carried out on a Kratos Kompact III spectrometer in the reflectron mode. Samples were deposited in a 2,5-dihydroxybenzoic acid matrix from acetone and doped with NaCl resulting in each species being observed as a Na$^+$ adduct and hence 23 amu greater than its molecular mass.

The figure shows the spectra from four different PMMA samples. In each case we observe an envelope of species, each separated by approximately 100 mass units, the molecular mass of the repeat unit in PMMA. The width at half height is typically 4–8 amu and the actual peak positions are accurate to within 1–2 amu. Number average (M_n) and weight average (M_w) molecular masses can be calculated easily from the spectra (Table 1).

The polymer prepared by GTP was terminated with water after 13 min giving an M_n of 4600 by GPC (Table 1). MALDI-TOF-MS [Fig. 1(*a*)] clearly shows the major species as

Table 1 Molecular weight information for PMMA from MALDI-TOF-MS and GPC. GPC measured in THF relative to PMMA narrow molecular weight standards at 1 ml min^{-1} on a Polymer Laboratories modular GPC system, polymers isolated by precipitation into hexane

	MS		GPC	
Polymerisation method	M_n	PDi	M_n	PDi
GTP	4160	1.03	4600	1.08
SAP	3400	1.08	5995	1.14
CCTP, AMBN (0.62 mass%)	1505	1.11	2266	1.43
CCTP, AMBN (6.2 mass%)	1572	1.19	2601	1.75

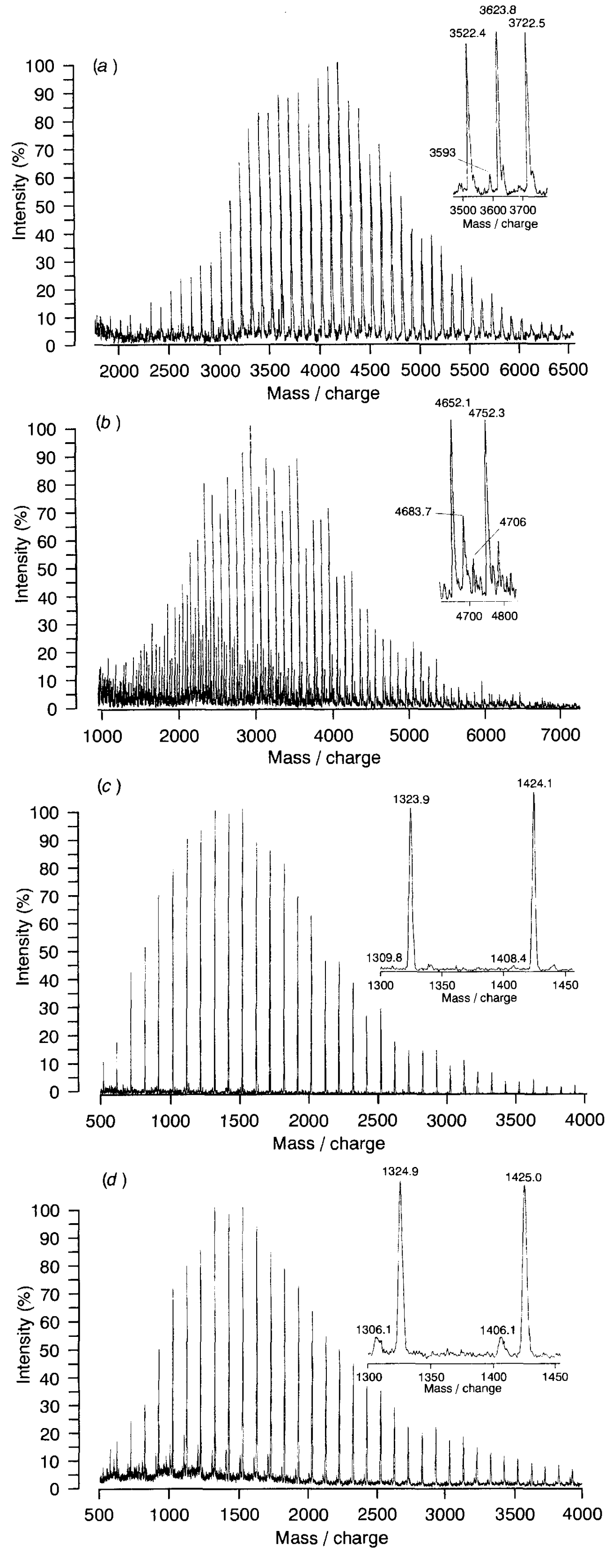

Fig. 1 MALDI-TOF-MS spectra of PMMA from GTP (*a*), SAP (*b*), CCTP 0.62 mass% AMBN (*c*) and 6.2 mass% AMBN (*d*). Inserts show expanded regions showing the repeat unit of PMMA, *ca.* 100 amu.

corresponding to a hydrogen end-group on both ends of the polymer **2**, however, there is also a small amount of end-group cyclisation, **3**, evidenced by the peaks at 31 amu below the major peaks, *i.e.* loss of MeO^- as would be expected for normal anionic polymerisation of methyl methacrylate.[9] SAP shows at least three different types of polymer [Fig. 1(*b*)]; the amount of each species can be controlled by changing the reaction conditions. The polymer **4** with butyl initiation, previously demonstrated by NMR,[10] and proton termination is not the dominant species under the reaction conditions, as expected. The major species is the butyl-initiated cyclic end-group terminated **5**. The third species is assigned to the *in situ* production of the butyl ketone **8** which copolymerises, effectively terminating the reaction. CCTP was carried out using **1** with both 0.62 mass% AMBN, [monomer]:**1** = 130000 [Fig. 1(*c*)] or 6.2 mass% AMBN [monomer]:**1** = 800000 [Fig. 1(*d*)]. In both cases the major product is seen to have been initiated with hydrogen as opposed to azo initiation from AMBN and termination is *via* hydrogen abstraction to yield **6** and Co^{III}–H, which is available for reinitiation.[9] Under forcing conditions with AMBN, azo initiation can be induced, seen as the smaller series in the spectrum [Fig. 1(*d*)], as a minor pathway leading to **7**, thus demonstrating the presence of normal radical initiation.

In conclusion it has been demonstrated that both end-groups of PMMA can be identified by MALDI-TOF-MS. This gives us the structure of each individual macromolecular species in the bulk polymer. This information is easily obtained and gives unique mechanistic information in addition to a measure of molecular mass averages. However, at present we are unsure as to the reason behind the discrepancies between the mass averages determined from both GPC and MALDI-TOF-MS. A possible explanation is that loss of small peaks at high molecular masses due to poor signal to noise lowers M_w whilst affecting M_n to a lesser extent, thus giving artificially narrow polydispersities. Mass spectrometry is gaining in usefulness for polymer characterisation, MALDI-TOF-MS has been shown to be extremely useful whilst being a remarkably simple and quick experiment to perform.

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References

1 D. H. Richards, G. C. Eastmond and M. J. Stewart, in *Telechelic Polymers: Synthesis and Applications*, ed. E. J. Goethals, CRC Press, Boca Raton, FL, 1989.
2 D. M. Hindenlang and R. D. Sedgwick, in *Comprehensive Polymer Science*, ed. G. Allen and J. C. Bevington, Pergamon, Oxford 1989, vol. 1, ch. 26, p. 573.
3 R. M. O'Malley, M. E. Randazzo, J. E. Weinzierl, J. E. Fernandez, L. N. Nuwaysir, J. A. Castro and C. L. Wilkins, *Macromolecules*, 1994, **27**, 5107.
4 R. P. Latimer, *Int. J. Mass Spectrom.*, 1983, **55**, 221.
5 R. P. Latimer and H. R. Schulten, *Int. J. Mass Spectrom. Ion Processes*, 1985, **67**, 227.
6 A. M. Belu, M. O. Hunt, J. M. DeSimonie and R. W. Linton, *Macromolecules*, 1994, **27**, 1905; X. K. Zhang, J. O. Stuart and S. J. Clarson, *Macromolecules*, 1994, **27**, 5229.
7 H. S. Creel, *Trends Polym. Sci.*, 1993, **1**, 336.
8 D. G. H. Ballard, R. J. Bowles, D. M. Haddleton, S. N. Richards, R. J. Sellens and D. L. Twose, *Macromolecules*, 1992, **25**, 5907.
9 T. P. Davis, D. M. Haddleton and S. N. Richards, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1994, **C34(2)**, 243.
10 D. M. Haddleton, A. V. G. Muir, J. P. O'Donnell, S. N. Richards and D. L. Twose, *Makromol. Chem., Macromol. Symp.*, in the press.