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Measurement of Propagation Rate Coefficients Using Pulsed-Laser Polymerization and Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry

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The IUPAC Working Party on modeling free-radical kinetics[1] noted that pulsed-laser polymerization (PLP) (e.g., ref 2) provides a means of measuring the propagation rate coefficient (k_p) that is virtually assumption-free. PLP involves pulsed-laser illumination of monomer and photoinitiator, under conditions such that a significant amount of macroradicals is terminated by a very short radical species formed in the pulse immediately subsequent to that in which the longer macroradical was formed. If one can identify the degree of polymerization ν_p of polymer terminated as above, then k_p is given by $\nu_p/[M]t_f$, t_f being the time between pulses and [M] the monomer concentration. This paper shows that matrix-assisted laser desorption/ionization (MALDI) mass spectrometry can be used to measured ν_p and provides an alternative to the only present means of carrying out this measurement, gel permeation chromatography (GPC).

Modeling polymerization under PLP conditions[2-4] shows that (i) ν_p can be identified as the point of inflection occurring at the lowest molecular weight in the number molecular weight distribution (MWD) of the formed polymer (this point of inflection is within a few percent of ν_p for all models for polymerization kinetics tested thus far) and (ii) ν_p also corresponds closely to the low-molecular-weight point of inflection on the weight MWD, and hence on a GPC trace.

Despite its advantages, PLP suffers from some major limitations, *inter alia* from the need to use GPC to identify ν_p. These include (i) the need for molecular-weight calibration, through either a reliable monodisperse standard or "universal" calibration and (ii) the necessity of accumulating sufficient polymer. Optimization with regard to these constraints is often opposed by having to ensure that (i) laser illumination of the sample is uniform (including negligible attenuation of the laser beam over the length of the sample cell); (ii) [M] changes negligibly over the course of the experiment[5,6] (both of which restrict the total amount of polymer that can be formed); (iii) a large proportion of polymer is formed by termination involving one chain that started in a given pulse and a second chain of a very low degree of polymerization that formed in the next pulse (as distinct from chain stoppage by termination between two chains that both have a large degree of polymerization, etc.); and (iv) the GPC is calibrated to provide accurate MWDs.

MALDI offers the potential for obtaining the number MWD directly and is applicable to polymers of moderate molecular weight (up to 10^5 under favorable conditions).[7,8] It is particularly applicable to low molecular weights (*ca.* 10^4), is an absolute method requiring no polymer molecular-weight calibration, and uses tiny quantities of sample (as low as picomolars). Since discrete oligomers can be resolved for masses $\lesssim 2 \times 10^4$, additional information is obtained on the monomer composition and end group of the material.[7-10] It may thus provide a means of determining ν_p for PLP that can overcome some disadvantages inherent in GPC. This paper tests this application, using a PLP sample which is cross-checked against GPC and which gives an accurate k_p.

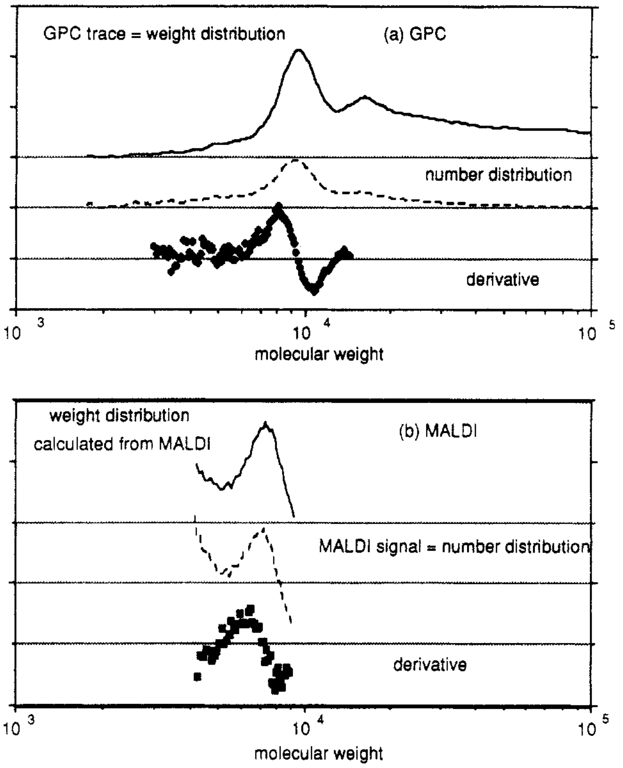

Figure 1. (a) GPC trace (full line), which is the weight MWD, number MWD (broken line) and derivative of weight MWD (points), for product from PLP of MMA at -8 °C, as described in the text. (b) Corresponding quantities for the same sample from MALDI, deduced from the data of Figure 2. All in arbitrary units.

PLP was carried out on a sample of methyl methacrylate (MMA) at -8 °C, in a 1-cm-diameter sample cell illuminated from below by the laser beam (a 308-nm Questek xenon chloride excimer laser operating at 35 mJ/pulse, pulsed at 15 Hz), following the design of Davis *et al.*[6] Samples were purged with argon for 2 min prior to photoinitiation, and postillumination radical activity was stopped with 2,4-di-*tert*-butylphenol. The photoinitiator was 7×10^{-4} mol dm^{-3} benzoin, and the MMA was undiluted. The sample length was *ca.* 1.5 cm, and the total beam attenuation was calculated to be *ca.* 50%. A sample was taken for analysis after 225 pulses; the resulting total conversion was less than 5%. Figure 1a shows the GPC trace from this sample (with the base line removed) analyzed using universal calibration[11] based on Polymer Laboratories styrene standards. The corresponding number MWD and derivative of the weight MWD are also shown. The maximum of this derivative is at 8200 (that for the number MWD differs by 100), corresponding to the low-molecular-weight point of inflection on the weight MWD. This yields ν_p, and thus k_p = 131 dm^3 mol^{-1} s^{-1}, in excellent accord with the IUPAC "recommended" value[1,12] of 134 dm^3 mol^{-1} s^{-1} at this temperature. This

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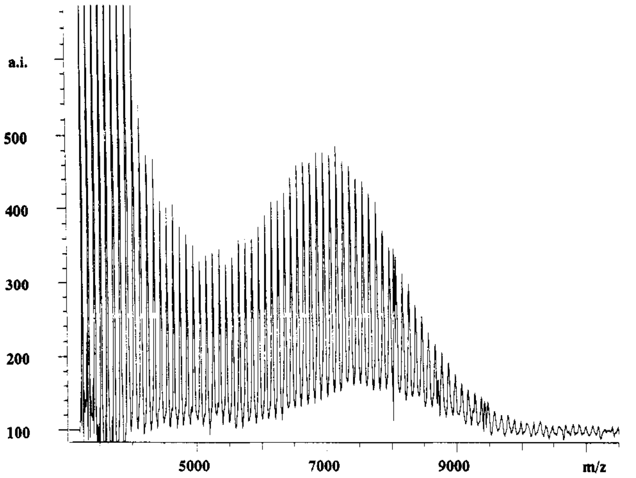

Figure 2. Matrix-assisted laser desorption/ionization time-of-flight mass spectrum for the product from PLP of MMA at −8 °C, as described in the text, acquired with pulse deflection of ions below m/z 3000.

suggests the reliable applicability of PLP analysis to the sample.

MALDI was performed on a Bruker REFLEX time-of-flight mass spectrometer, operating with an acceleration voltage of +20 kV and detection in the reflectron mode. The sample (1.3 mg) was dissolved in 100 μL of acetone, and 2 μL of this was mixed with 10 μL of matrix solution composed of 0.1 mol dm^{-3} of 2,5-dihydroxybenzoic acid in 1:1 (v/v) water/acetonitrile. To this was added 2 μL of 10^{-1} mol dm^{-3} of NaCl in water. Approximately 2 μL of this mixture was placed on the probe and dried, giving a total sample load on the probe of 75 pmol. This was then irradiated with an N_2 laser wavelength of 337 nm at 5 Hz with a total accumulation of 200 shots per spectrum at slightly above threshold power for ion formation (10^6–10^7 W cm^{-2}).

Figure 2 shows the MALDI mass spectrum of the same sample used for the GPC analysis of Figure 1a. The peaks in the spectrum are molecular ions formed by the attachment of Na^+ to pMMA oligomers; the resulting spacing between the peaks is m/z 100, corresponding to the molar mass of MMA. Peak heights were measured after base-line correction and the data then smoothed. Figure 1b shows the resulting number MWD, calculated weight MWD, and derivative calculated from the three-point smoothed weight MWD. The inflection point at 6100 ± 300 is very apparent.

The discrepancy of 2000 in 8000 can be ascribed to a number of sources. One of these is that low-molecular-weight "monodisperse" GPC calibration standards, when analyzed by MALDI, sometimes show significant polydispersity with a peak up to 40% lower than that claimed.[8] In general, polymer molecular weight by MALDI is shown to be within 5–10% of the values given by GPC.[8,9] Thus inaccuracies in the polymer standards for the GPC could lead to this error in assigning the molecular weight of the PLP sample. Additionally, decreased detector response with increasing molecular weight was suspected as also playing a role in the lower value from MALDI. However, this is not a large factor here because we are at high acceleration potential (Bahr *et al.*[9] found that the $\langle M_n \rangle$ value increases 10% with postacceleration voltages from 3 to 12 kV; above 12 kV it remains constant to 20 kV; in the present study, the ions strike the detector with an energy of 21.5 keV, so this effect is minimal). Furthermore, the difference in sensitivity over this narrow m/z range (6000 *vs* 8000) is small.[13,14]

This work shows that MALDI has the sensitivity to give a sufficiently precise point of inflection in the MWD obtained from pulsed-laser polymerization and therefore can provide a method of obtaining propagation rate coefficients in a way that obviates some of the disadvantages of GPC analysis.

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