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Determination of the Propagation Rate Coefficient (k_p) and Termination Mode in the Free-Radical Polymerization of Methyl Methacrylate, Employing Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry for Molecular Weight Distribution Analysis

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Introduction. Pulsed laser polymerization (PLP) has been shown to be the most accurate method for determining the propagation coefficient (k_p) in free-radical polymerization by a number of groups.[1−7] The success and reliability of the PLP method has been recognized by an IUPAC working party on modeling free-radical polymerization kinetics,[8] and this has led to a general recognition of PLP as the primary experimental approach to propagation rate coefficients. The PLP technique consists of pulsing UV-laser light at a known frequency through a solution of monomer with a suitable photoinitiator added. By analysis of the resulting molecular weight distribution (MWD), the rate coefficient k_p can be found. This method is unique in that the kinetic analysis is largely free from model-based assumptions. The kinetic analysis of PLP collapses into a single equation (1).

$$\nu = k_p[\mathrm{M}]t_0 \tag{1}$$

Here the kinetic chain length (v) is proportional to the monomer concentration, the flashing frequency (t_0), and the propagation rate coefficient. Thus if v can be determined from experiment, k_p can be calculated. From previous work[6] the chain length, v, can be best approximated as the low molecular weight inflection point on a GPC chromatogram. Thus accurate MWD analysis is extremely important if reliable k_p values are to be obtained.

GPC has been firmly established as a procedure for determining MWD's; however, in its basic form, it is not an absolute technique and is subject to calibration errors. It is obvious that the PLP method would benefit greatly if there was an alternative to GPC-MWD analysis. Danis et al.[9] suggested the use of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) for MWD analysis. Their work yielded a propagation rate coefficient significantly at odds with that obtained from GPC data. The reason for this discrepancy was not determined, and thus it was unclear whether MALDI-MS could be used for accurate kinetic analyses. Danis et al.[9] suggested that this discrepancy may have its origin in poor GPC calibration resulting from incorrectly assigned standards. However, this is unlikely as reputable standards suppliers use well-established techniques such as light scattering and osmometry to characterize their products. Although MALDI as an ionization method seems to be insensitive to mass,[10] there is growing evidence that TOF with electron multiplier detection is mass sensitive.[11] This does result in low-mass macromolecules being observed in preference to high-mass macromolecules, adversely affecting M_w in polymers with polydispersity greater than about 1.2 in MALDI-TOF-MS. The aim of the work reported here was to optimize the PLP/MALDI-TOF-MS experiment to find an operating window for accurate kinetic data determination.

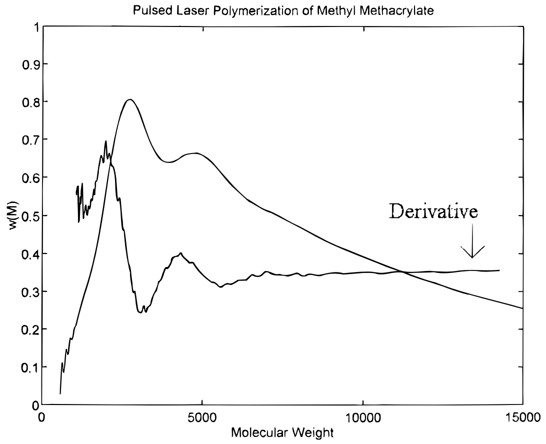

Figure 1. Weight molecular weight distribution analysis from GPC of a PLP-derived polymer with derivative overlay.

Experimental Procedures. *Materials.* Methyl methacrylate (MMA) was purified in the usual way[12] and charged to a quartz ampule with solvent (toluene) and the photoinitiator azobis(isobutyronitrile) (AIBN). The solution was degassed by purging with argon for 2 min and subsequently polymerized at 0.2 °C by a pulsed 308 nm excimer laser (XeCl) with constant pulse frequency. The experimental setup employed was similar to that of Davis et al.[1] Polymerization was ceased by precipitation of the polymer into hexane.

Matrix-Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) Mass Spectrometry. Mass spectrometry was carried out on a Kratos Kompact III MALDI-TOF mass spectrometer (Kratos, Manchester, UK), incorporating a 337 nm nitrogen laser with a 3 ns pulse duration and an electron multiplier detector. The instrument was operated in the positive ion reflectron mode with an accelerating potential of +20 kV. The mass scale was calibrated using bovine insulin with 2,5-dihydroxybenzoic acid as the matrix along with NaCl. For each sample, the spectra were averaged over 175 laser shots. Careful modification of the laser power was required to operate at the threshold energy.

MALDI-TOF Sample Preparation. A 0.5 μL sample of the matrix solution (0.1 M 2,5-dihydroxybenzoic acid in 50/50 acetone−water solution with added salt (NaCl)) was deposited on the stainless steel sample slide. The matrix solvents were allowed to evaporate off under a stream of air with occasional stirring to induce fine crystal growth. The PMMA sample was diluted with THF such that each solution contained approximately 0.1 mg/mL. A 0.5 μL of this polymer solution was then deposited on top of the matrix, and the solvents were evaporated off.

Results and Discussion. The GPC analysis of the laser-polymerized polymer is shown in Figure 1 with the derivative overlay. The point of inflection on the low-MWT side of the GPC distribution appears as the maximum of the derivative overlay. In the case shown

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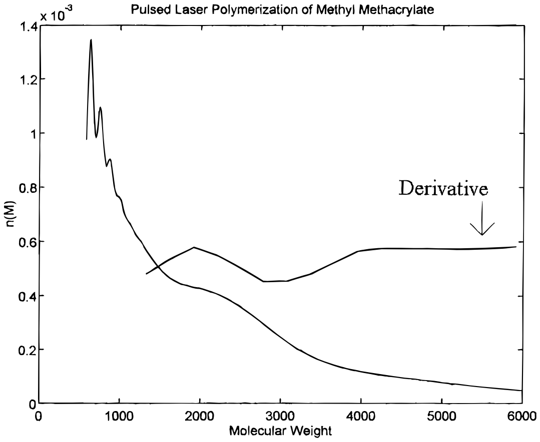

Figure 2. Number molecular weight distribution from GPC analysis with derivative overlay.

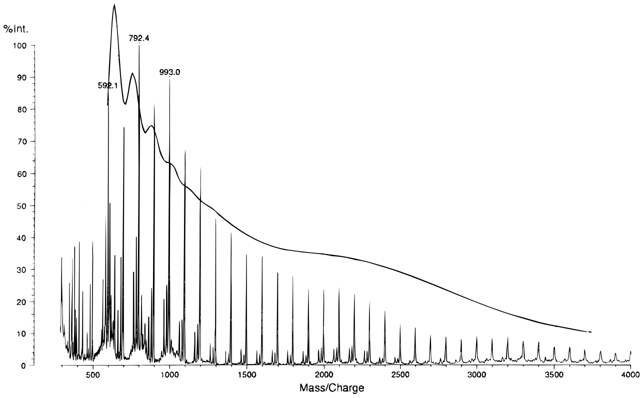

Figure 3. Number molecular weight distribution from GPC analysis overlayed on a MALDI-TOF mass spectrum.

here, this point appears at a MWT of 2000, or 20 kinetic chain units of MMA, yielding a k_p for MMA at 0.2 °C of 170 mol/(L.s), which agrees with an earlier value.[13] To transform the chromatogram to a number molecular weight distribution eq 2 was used as suggested by Hutchinson et al.[14]

$$n(M) = w(M)/M \tag{2}$$

In Figure 2, the transformed chromatogram trace and its derivative overlay show a typical number distribution for a PLP-derived polymer. The point of inflection is taken at the low-MWT inflection point of the distribution, giving rise to the derivative maximum which coincides with the midpoint of the plateau of the number distribution. This again occurs at 2000 MWT or 20 kinetic chain units of MMA, giving the same k_p value as above. An illustration of the congruence of the GPC chromatogram and the MALDI-TOF spectrum is shown in Figure 3, which depicts the number distribution from Figure 2 overlaid on the MALDI-TOF analysis of the same polymer. The critical point of the GPC number distribution (i.e., the point of inflection) is clearly evident at the same molecular weight on the MALDI-TOF-derived molecular weight distribution envelope. MALDI-TOF yields exactly the same propagation rate coefficient. This result comprises the first reliable, reproducible, and accurate determination of k_p from a MWD analysis other than GPC.

It should be noted that the important feature in PLP is a specific point on the MWD. In GPC analysis, the chromatogram appears as a continuous distribution and the point of inflection can easily be obtained from the derivative. In MALDI-TOF analysis, resolution is enhanced and discrete polymer chains can be seen. Clearly, the point of inflection is not necessarily identified by a discrete oligomer (because of Poisson broadening). This can make identification of the inflection point in MALDI-TOF a harder facet to resolve.

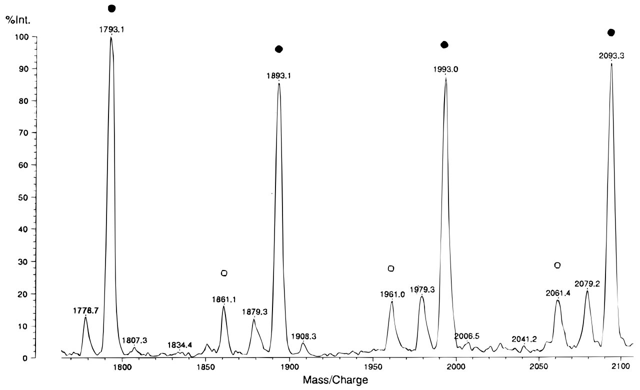

Figure 4. Expansion of point of inflection region of MALDI-TOF mass spectrum (see text for explanation).

It may be of interest to report that it is possible to access some information on the termination mechanism by chain end analysis. Figure 4 is an expansion of the region surrounding the inflection point on the MALDI-TOF MWD analysis. There are essentially two series in this mass spectrum. The peaks labeled with a full circle are those corresponding to sodium adduct oligomers with a single initiator fragment per molecule, and the peaks labeled with an empty circle are those corresponding to sodium adduct oligomers with two initiator fragments per molecule. The peaks at 1778, 1879, 1979, etc. correspond to lithium adducts of the former series (lithium is present as an impurity in the cation source used). The oligomer used for calculation is at 2093.3 DA, i.e., oligomer MWT = 2093.3 − 68.1 − 22.9 = 2002 Da. (AIBN initiator fragment = 68.1 Da and Na^+ = 22.9 Da). Therefore $v = 20$.

Thus some indication of termination mode is available for this PLP-derived polymer. By integrating the appropriate peaks, k_{td}/k_{tc} can be determined and in this case is found to equal 2.5. This number does not represent the true k_{td}/k_{tc} ratio for the polymerization process as all the integrated peak areas across the spectrum would be needed to be accounted for. However, at this particular point of the spectrum, the bulk of the chains have undergone a termination process occurring at a laser flash. Thus termination at this point is dominated by a large radical/small radical termination event. This is probably not primary radical termination as Moad et al.[3] have suggested that very little primary radical termination occurs in PLP. The number given above does suggest that abstraction dominates as the termination mechanism. In fact, the ratio of the peak areas representing chains with one or two initiator fragments does not vary greatly across the distribution. The issue of whether MALDI-TOF can be used qualitatively to obtain chain end information has been established in earlier work.[15] However, it remains to be proven whether quantitative analysis of chain ends can be claimed with confidence, and we are currently running experiments on model compounds to establish this fact.

This work shows that it is possible to determine k_p for the free-radical polymerization of MMA using a combination of pulsed laser initiation and MALDI-TOF analysis. The result we obtain for k_p concurs exactly with that derived from GPC analysis. It also shows that termination mode information is accessible, and in the case of AIBN-initiated PLP of MMA, the termination mode appears to be dominated by abstraction.

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