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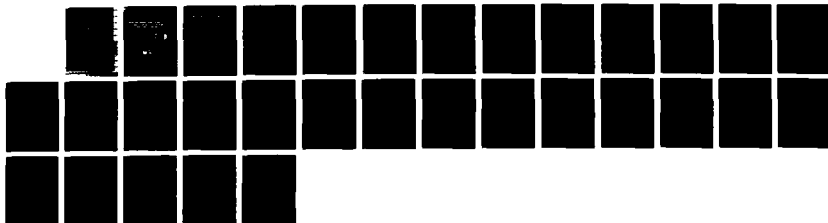
MOLECULAR WEIGHT DETERMINATION OF ENERGETIC POLYMERS BY 1/1
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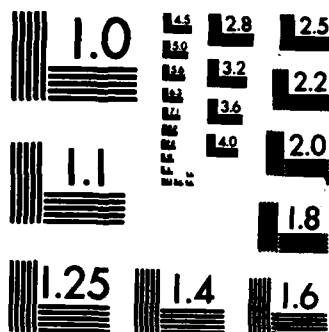
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Molecular Weight Determination of Energetic Polymers by Low-Angle Laser Light Scattering

by
R. J. Cramer
Research Department

FEBRUARY 1987

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FOREWORD

Knowledge of the molecular weight and molecular weight distributions of polymeric energetic binders is essential in designing the cure behavior and the mechanical and physical properties of solid propellants. Accurate and absolute molecular weights for new propellant binders are determined with difficulty by conventional gel permeation chromatography which relies upon known calibration standards, and in the area of new energetic materials with exotic compositions, appropriate calibrations standards are not available. Through the use of low-angle laser light scattering techniques, absolute molecular weights and molecular weight distributions of polymers can be accurately determined without the use of standards. We have acquired the appropriate gel permeation chromatography and light scattering instrumentation and methods for characterization of energetic polymers with a range of molecular weights have been developed.

This work was carried out from March to August 1986 under the Advanced Energetic Binders program. This interim report describes the technique and summarizes the results obtained on energetic polymers currently being evaluated in solid-fuel propellants. This report has been reviewed for technical accuracy by Geoffrey A. Lindsay and Robert B. Green.

Approved by
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Research Department
5 February 1987

Under authority of
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(U) Accurate and absolute molecular weights for new propellant binders are determined with difficulty by conventional gel permeation chromatography (GPC) which relies upon known calibration standards. Absolute molecular weight and molecular weight distributions of energetic binders (GAP and polyoxetanes) were determined using GPC and low-angle laser light scattering (LALLS). This technique yields molecular weight directly without the need of calibration standards; molecular weights as low as 700 can be effectively analyzed by the LALLS technique.					
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INTRODUCTION

Second only to polymer composition, the parameters of greatest influence on physical properties of energetic polymers are the average molecular weight and molecular weight distribution. This report describes the measurement of the molecular weight and molecular weight distribution of various energetic polymers, such as glycidyl azide polymer (GAP) and the substituted polyoxetanes using gel permeation chromatography (GPC) or size exclusion chromatography (SEC) with a low-angle laser light scattering (LALLS) detector coupled with a differential refractive index (DRI) detector.

The separation of components in a polymer sample by GPC is primarily a result of steric exclusion of the polymer molecule or a difference in molecular size of the components in solution, where the larger molecules are found in the early elution volume and the smaller molecules elute last (Reference 1). The molecular size or the hydrodynamic radius, in turn, depends upon molecular weight, chemical composition, molecular structure and the experimental parameters (solvent, temperature, and pressure) (Reference 2). Therefore, when calculating an accurate molecular weight and molecular weight distribution for a polymer system using GPC calibrated with standards, one must select standards within the same molecular weight range, chemical composition, and structure as the polymer sample of interest (Reference 3). Often an appropriate standard is not available, particularly in the case of new energetic binders, and one risks errors in molecular weight calculations if the change in the molecular size/weight relationship is not linear.

Through the use of LALLS in combination with a concentration detector (i.e., refractive index, IR, or UV), accurate molecular weight information can be obtained without relying upon calibration standards (Reference 4).

The parameter of interest in a light scattering measurement is the Rayleigh factor, R_θ , which is determined as

$$R_\theta = (P_\theta/P_0) (D/\sigma' l') \quad (1)$$

where P_θ is the intensity of scattered light and P_0 is the intensity of the incident light, D is the transmittance of the measuring attenuators employed during the recording of P_0 , σ' is the solid angle through which the scattered light is collected, and l' is the length parallel to the incident beam of the scattering volume (Reference 5). Since σ' and l' are constants determined by the geometry of the instrument, and since D can be optically determined, R_θ can be found without

recourse to standards. Tabulations of σ' and l' are available and D is determined during instrument calibration using a solvent with a known Rayleigh factor, such as toluene (Reference 6).

At the small forward scattering angle between 2 and 7 degrees, at only one angle, and at low solute concentrations, the relationship between the Rayleigh factor and weight-average molecular weight is

$$Kc/\bar{R}_\theta = 1/\bar{M}_w + 2 A_2 C \quad (2)$$

Equation 2 is the fundamental LALLS equation which forms the basis of the method for molecular weight determinations of polymers by LALLS. The "excess" Rayleigh, $\bar{R}_\theta$, is the difference in the Rayleigh factor between the solution and that of the solvent.

$$\bar{R}_\theta = R_{\text{solution}} - R_{\text{solvent}} \quad (3)$$

The polymer optical constant K in Eq. 2 is defined for a polarized laser light source as

$$K = (2 \pi^2 \eta^2 / \lambda^4 N) (dn/dc)^2 (1 + \cos^2 \theta) \quad (4)$$

where η is the refractive index of the solution at the incident wavelength, λ , N is the Avogadro's number, and θ is the angle of scattered light. The term dn/dc is known as the specific refractive index increment or differential refractive index increment and is the change of the solution refractive index as a function of solute concentration at a given wavelength, temperature, and pressure (Reference 7).

The dn/dc reflects the optical characteristics of the polymer and solvent, their differences in optical polarizability, and depends upon the chemical compositions of both components (Reference 8).

In a separate experiment, a differential refractometer with λ equal to that used in measuring the Rayleigh factor is used in determining the dn/dc (Reference 9).

To determine the second virial coefficient, A_2 in Equation 2, measurements of $\bar{R}_\theta$ are made for a series of solutions of different concentrations. Upon constructing a plot of $Kc/\bar{R}_\theta$ versus concentration, A_2 is found as one-half the slope of the line.

For measurement of the $\bar{M}_w$ and molecular weight distributions, the LALLS instrument is connected in a series with the GPC columns and the DRI detector (see Figure 1). The molecular weight at uniform intervals on the GPC elution curve is then calculated from the fundamental LALLS equation (Equation 2). With adequate GPC resolution, each point along

the DRI curve represents a species of concentration, C , and monodispersed molecular weight, M_w (see Figure 2). The refractive index and R_θ are recorded simultaneously, and since the scattering is geometrically defined, the molecular weights are absolute.

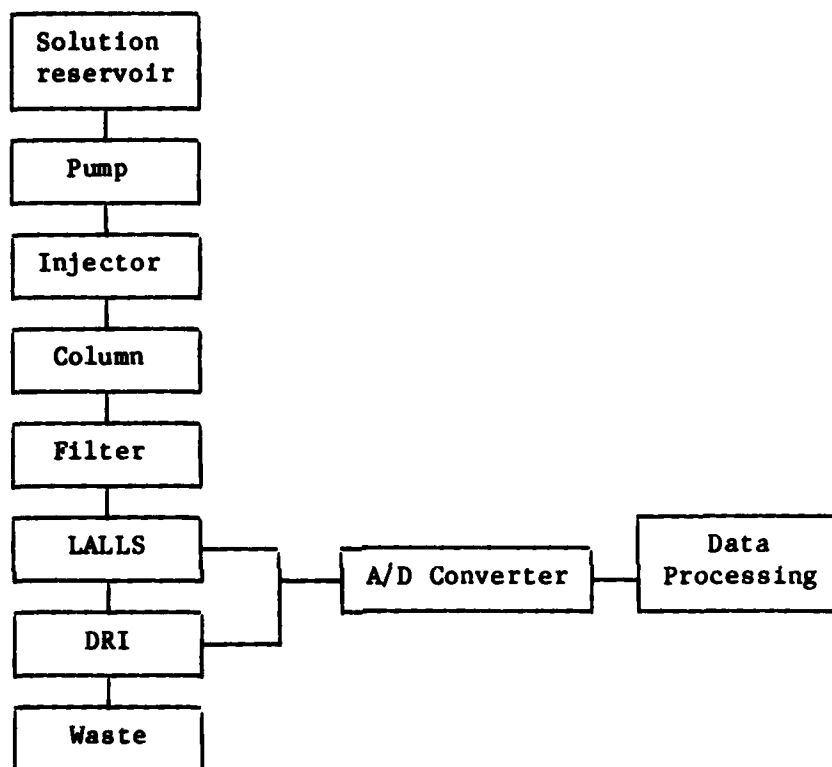


FIGURE 1. Instrumentation Configuration for the Determination of Molecular Weights by GPC/LALLS.

Once this molecular weight data has been collected, the molecular weight averages, $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$, the number-average, weight-average, and z-average molecular weights can be calculated in the convenient manner:

$$\bar{M}_n = \frac{\sum C_i}{\sum (C_i/M_i)} \quad (5)$$

$$\bar{M}_w = \frac{\sum (C_i M_i)}{\sum C_i} \quad (6)$$

$$\bar{M}_z = \frac{\sum (C_i M_i^2)}{\sum (C_i M_i)} \quad (7)$$

Hence, with knowledge of the two polymer constants, the refractive index increment and the second virial coefficient, and through the

measurement of $\bar{R}_\theta$ and concentration along a GPC elution curve, molecular weights can be determined for any soluble polymeric material.

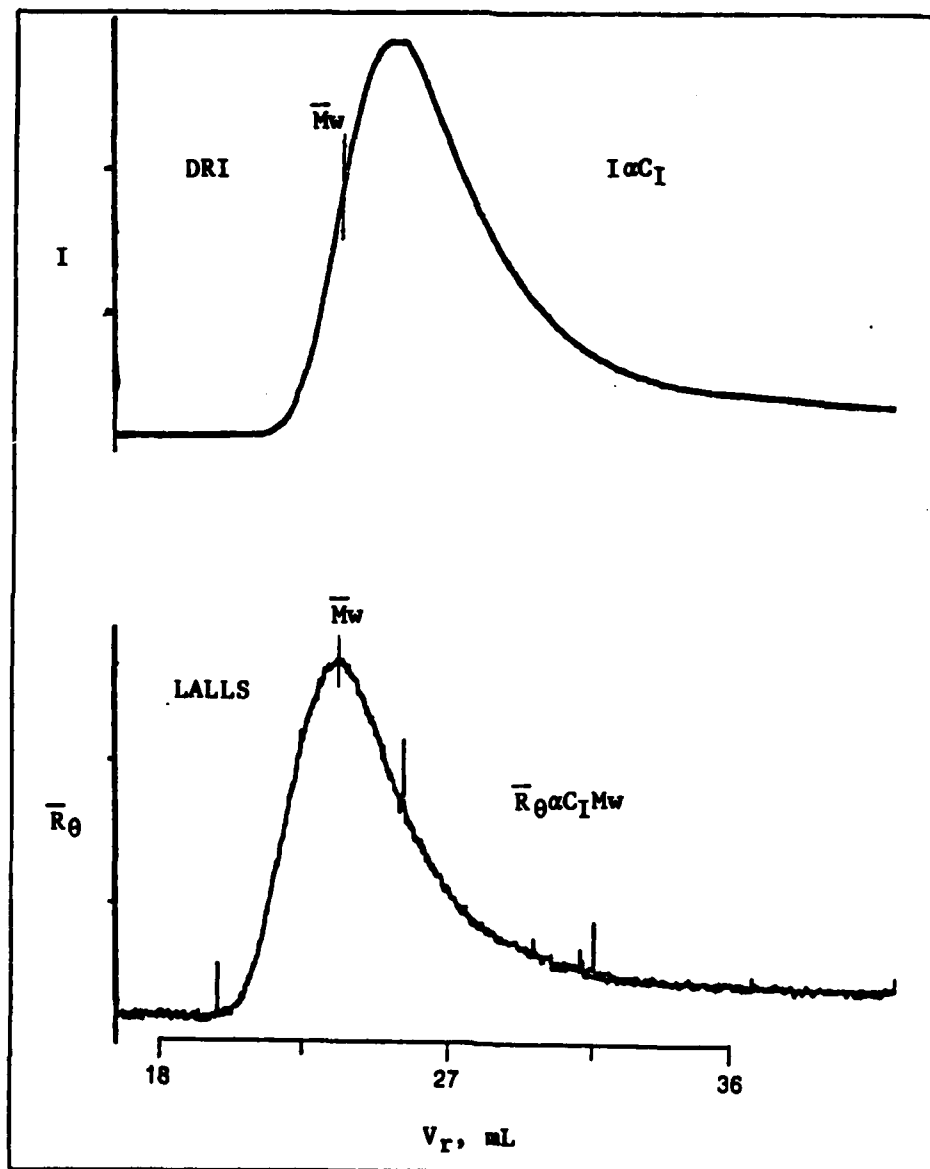


FIGURE 2. Example of a Typical GPC DRI and LALLS Response.

EXPERIMENTAL SECTION

MATERIALS

The solvent HPLC grade tetrahydrofuran from Aldrich Chemical Company, Milwaukee, Wis., was used directly without further purification.

INSTRUMENTATION AND METHOD

The specific refractive index increments were measured at 30°C on stock solutions with known concentrations in the range of 15 to 40 mg/mL with a KMX-16 laser differential refractometer calibrated against NaCl solutions.

The off-line (static) values of A_2 were measured using the stock solutions above, at 6 to 7 degrees forward scattering angle, and 0.2 field stop. Texas Instrument linear regression analysis was used for the calculation of A_2 from a plot of Kc/R_θ versus concentration.

The polymer separations and molecular weight determinations were carried out with a Beckman 112 solvent delivery module connected to a Rheodyne 210 injector equipped with a 100 μ L injection loop. Altex spherogel 1000 and 500 Å columns with a molecular weight range of 500 to 50 000 were connected in series. Tetrahydrofuran was the mobile phase used throughout, prefiltered through 0.50 Millipore filters at 0.5 mL/min flow rate at ambient temperature. Concentration of eluent was detected by an Altex 156 refractive index detector. The light scattering data was collected on a KMX-6 LALLS instrument at 6 to 7 degrees forward scattering annulus and 0.2 field stop, mounted with a stainless steel GPC cell with a 5-millimeter flow-through cell. The data from both detectors was acquired through an analog/digital CMX-10 dual interface module and processed on a Chromatix CMX-160 or a VT-125 using software package NWCWT3.

RESULTS AND DISCUSSION

MOLECULAR WEIGHT ANALYSIS OF POLYOXETANES

The polyoxetanes evaluated along with a brief description of the polymer samples are given in Table 1. The dn/dc values, polymer optical constants, and second virial coefficients that were determined and used as parameters for the molecular weight calculations are listed in Table 2. The molecular weights determined by GPC/LALLS are given in Table 3; Figures 3 through 7 show the GPC/LALLS response curves for the polyoxetane samples analyzed.

TABLE 1. Evaluation of Polyoxetanes.

Number	Polymer	Comments
I	BAMO/NMMO, F = 2	BAMO/NMMO, ~70/30
II	BAMO/NMMO, F = 2 646-25	Prec. into MeOH, insol fraction
III	BAMO/NMMO, F = 3	BAMO/NMMO, ~70/30
IV	BAMO/NMMO, F = 3 646-23	Prec. into MeOH, insol fraction
V	PolyNMMO, 646-18	Batch 2 in NMMO polymer series

TABLE 2. PolyNMMO and BAMO/NMMO Copolymers, dn/dcs, Polymer Optical Constants, and Second Virial Coefficients.

Polymer	Specific refractive index increments, dn/dc (mL/g)	Polymer optical constants, K (mol-cm ² /g ²)	Second virial coefficients A ₂ (mol-mL/g ²)
BAMO/NMMO, F = 2	0.0988	7.89×10^{-8}	1.65×10^{-3}
BAMO/NMMO, F = 3	0.0815	5.35×10^{-8}	8.7×10^{-4}
PolyNMMO	0.0615	3.43×10^{-8}	1.34×10^{-3}

TABLE 3. Molecular Weights of PolyNMMO and BAMO/NMMO Copolymers.

Polymer	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
BAMO/NMMO, F = 2	7 400	4 500	1.64
BAMO/NMMO, F = 2 (646-25)	28 600	15 300	1.87
BAMO/NMMO, F = 3	25 700	14 100	1.83
BAMO/NMMO, F = 3 (646-23)	33 500	18 500	1.81
PolyNMMO (646-18)	10 200	7 000	1.45

PolyNMMO (II) was found to have a lower specific refractive index increment and a correspondingly lower polymer optical constant than the difunctional polyBAMO/NMMO 70/30 copolymer (I). It is also interesting to note that the magnitude of the dn/dc for the trifunctional polymer (III), which was also prepared to have a comonomer ratio of 70/30 based on the monomer feed during polymerization, is lower than expected. Since the dn/dc value is dependent upon the copolymer composition (Reference 10), the dn/dc value indicates the NMMO content is higher

than expected. Fourier transform infrared (FTIR) results have shown, in fact, the BAMO/NMMD copolymer composition to be 60/40 (Reference 11). Thus, in these systems, the magnitude of the dn/dc values give information as to the NMMD content in the copolymer.

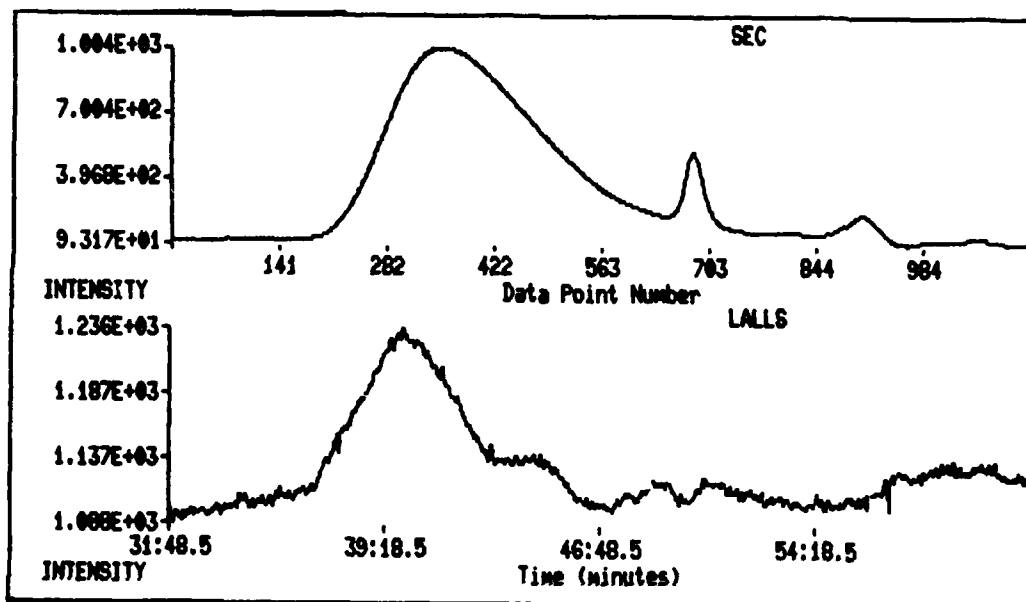


FIGURE 3. BAMO/NMMD Copolymer, $F = 2$, GPC/LALLS Chromatograph.

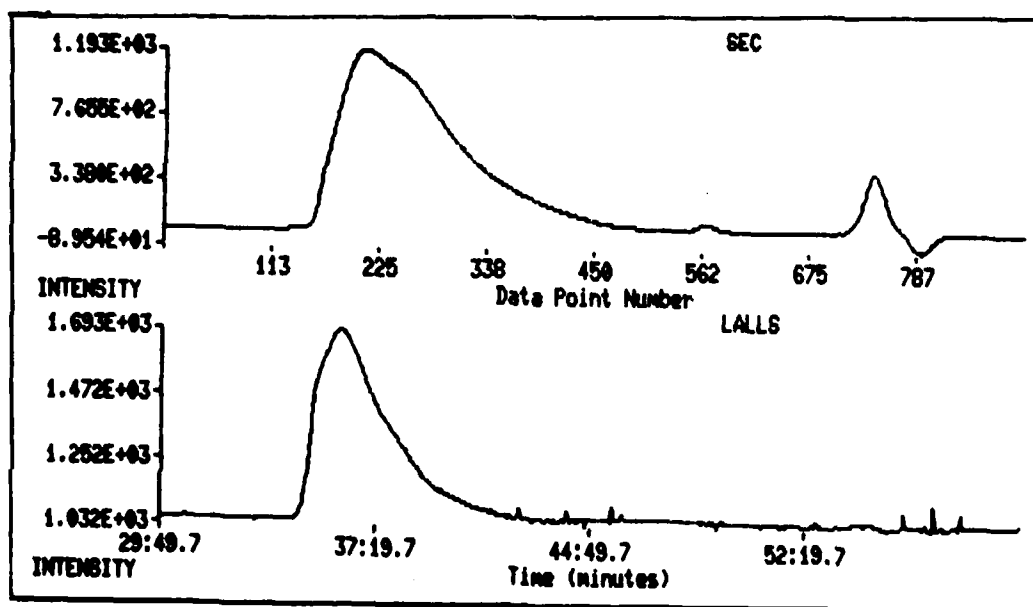


FIGURE 4. BAMO/NMMD Copolymer, $F = 2$ (646-25), GPC/LALLS Chromatograph.

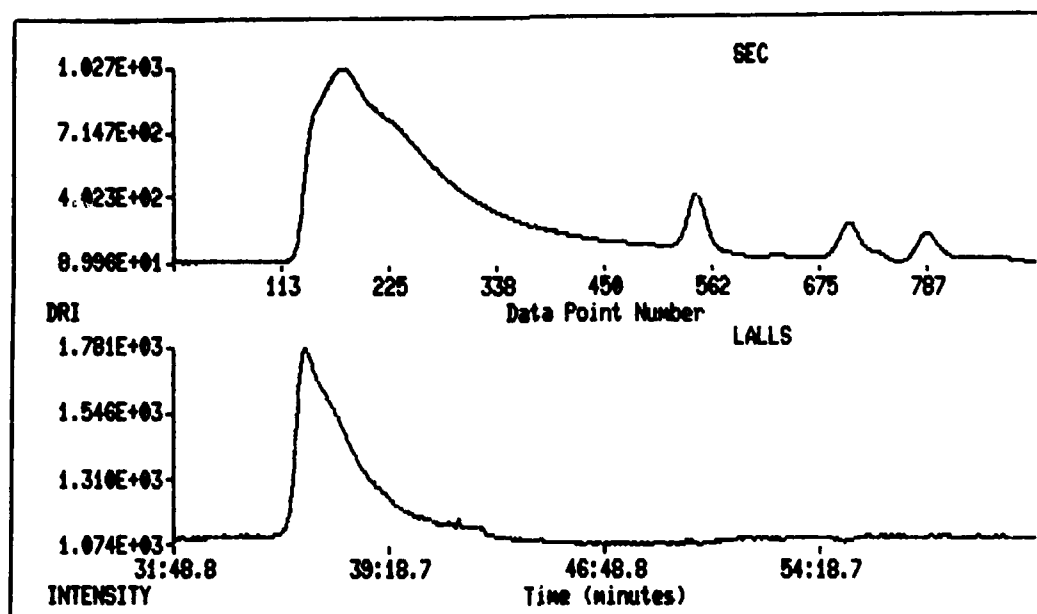


FIGURE 5. BAMO/NMMO, F = 3, GPC/LALLS Chromatograph.

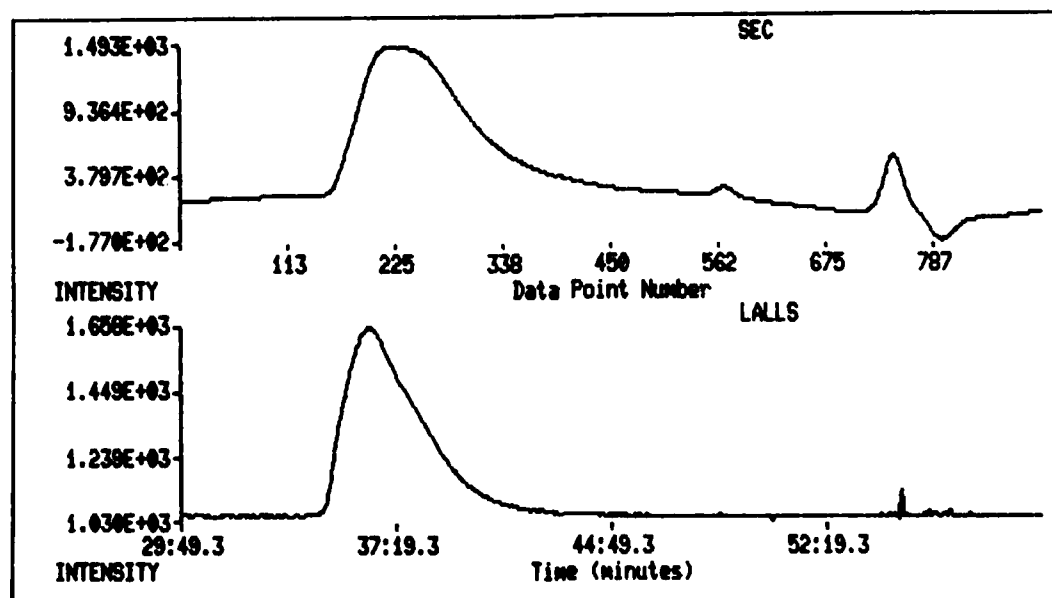


FIGURE 6. BAMO/NMMO Copolymer, F = 3 (646-23), GPC/LALLS Chromatograph.

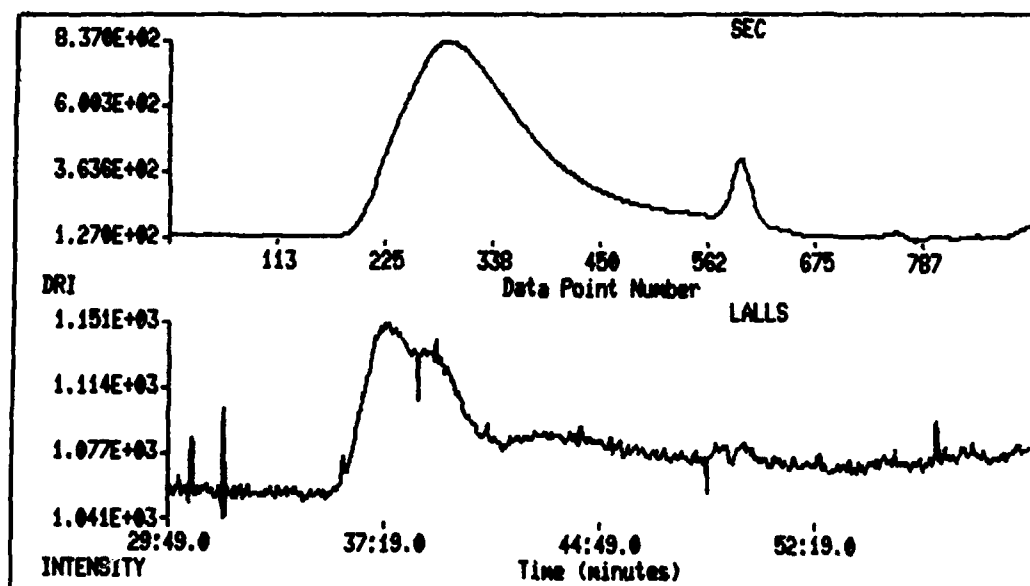


FIGURE 7. PolyNMMO (646-18) GPC/LALLS Chromatograph.

All of the samples are rather polydisperse systems and are skewed on the low molecular weight elution volume (towards the right). Figures 3 and 5 also show the presence of oligomeric impurities as sharp peaks. The levels of these impurities are reduced somewhat in Figures 4 and 6 by washing the product with MeOH. The discontinuity in the decreasing concentration slope in the LALLS data in Figure 3 implies a bimodal molecular weight distribution. If a shoulder occurs when the concentration detector is decreasing, the eluant molecular weight must be increasing. This increase in molecular weight with increasing retention volume demonstrates an inconsistency in the molecular weight-to-hydrodynamic size relationship. A comparison of polymers that have different polymer densities, such as copolymers with different compositions, but nearly equivalent hydrodynamic volumes, will show a difference in molecular weight (Reference 12). The case may be that the second molecular weight distribution in Figure 3 can be attributed to a series of copolymers containing high BAMO content.

Branching is evident from the high molecular weight shoulder in the SEC curve of Figure 5, but not as evident in Figure 6 which has been washed with MeOH. Also, in the trifunctional polymers, some of the low molecular weight material is removed by the MeOH wash without affecting the molecular weight distribution. The slope of the leading edge of the LALLS in Figures 5 and 6 is much steeper than the SEC counterpart. A qualitative appraisal of the two chromatograms indicates the presence of high molecular weight components at the sample elution front.

In Figure 7, LALLS shows three, possibly four different modes of molecular weight distribution at the high molecular weight end which are not evident if one evaluates the SEC concentration response alone. These various modes may be caused by branching, the presence of polymers with different end groups, or macrocyclic impurities present in the mixture. This is a prime example which illustrates the benefits of LALLS information. If one relies upon the SEC curve alone, it would be assumed that the broad distribution consists of linear polymer with an increasing molecular weight. The LALLS response curve indicates that this is not the case.

MOLECULAR WEIGHT ANALYSIS OF GAP AND PECH

The GAP and PECH samples analyzed are listed in Table 4 along with the equivalent weights as determined by titration at Rocketdyne, Canoga, Park, Calif., the dn/dc , corresponding polymer optical constants, and the second virial coefficients. The samples are listed in an order where PECH is precursor to the corresponding GAP, i.e., 0337-158 was prepared from HX101, etc.

TABLE 4. GAP and PECH Specific Refractive Index Increments, Polymer Optical Constants, and Second Virial Coefficients.

Sample	Equiv. Weight	Specific refractive index increments, dn/dc (mL/g)	Polymer optical constants, K (mol cm^4/g^2)	Second virial coefficients, A_2 (mL-mol/g ²)
GAP				
0337-158	541	0.091	6.71×10^{-8}	0.00
0337-165	768	0.091	6.67×10^{-8}	3.83×10^{-3}
0337-181	1962	0.102	8.30×10^{-8}	2.40×10^{-3}
200-2A	1231	0.096	7.35×10^{-8}	1.42×10^{-3}
0337-167	1148	0.097	7.51×10^{-8}	2.69×10^{-3}
PECH				
HX101	508	0.082	5.44×10^{-8}	0.00
L9620	400	0.075	4.55×10^{-8}	0.00
L9654	1830	0.085	5.75×10^{-8}	0.00
HX102P	1076	0.089	6.34×10^{-8}	0.00
LX392	1070	0.086	5.91×10^{-8}	0.00
L9621	680	0.078	4.93×10^{-8}	0.00
3M L9916	...	0.085	5.78×10^{-8}	2.16×10^{-3}

The dn/dcs for GAP were found to be higher than the dn/dcs of PECH, which is important when considering that the light scattering intensity

depends upon the square of the dn/dc , and greater sensitivity in the molecular weight determinations of GAP would be expected over PECH at the same molecular weight. Also, the GAP dn/dcs increase with increasing equivalent weight. Figure 8 shows a plot of dn/dc versus GAP equivalent weight; at higher equivalent weights, the dn/dc appears to approach a limiting value. The dn/dc usually depends upon the molecular weight for low M and attains a limiting constant for sufficiently high M (Reference 13). This suggests that for a new GAP product for which the dn/dc is not known, the dn/dc should be measured prior to the calculation of average molecular weights to ensure the use of an accurate polymer constant. Alternatively, the dn/dc may be estimated for a new GAP system by the use of Figure 8 as a dn/dc calibration curve if the equivalent weight is known.

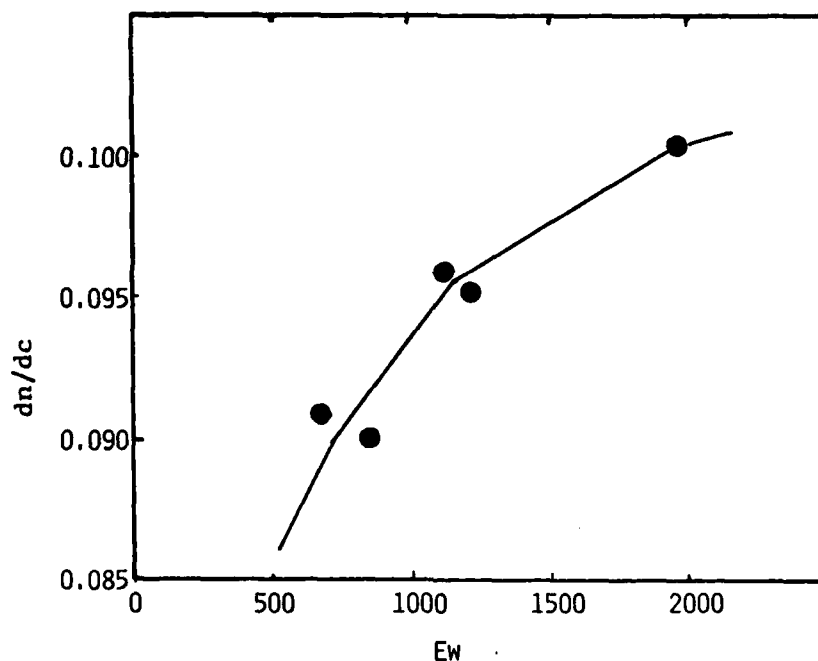


FIGURE 8. A Plot of Equivalent Weight Versus the dn/dcs Found for GAP Samples in THF.

The second virial coefficients were calculated from the static LALLS experiments; the plots of $Kc/\bar{R}_0$ for the GAP samples are shown in Figures 9 and 10. Those samples listed with an A_2 of zero essentially showed no increase in $Kc/\bar{R}_0$ with concentration.

The average molecular weights, the polydispersity index, and the functionality calculated from the reported titration equivalent weights and LALLS number-average molecular weight are presented in Table 5.

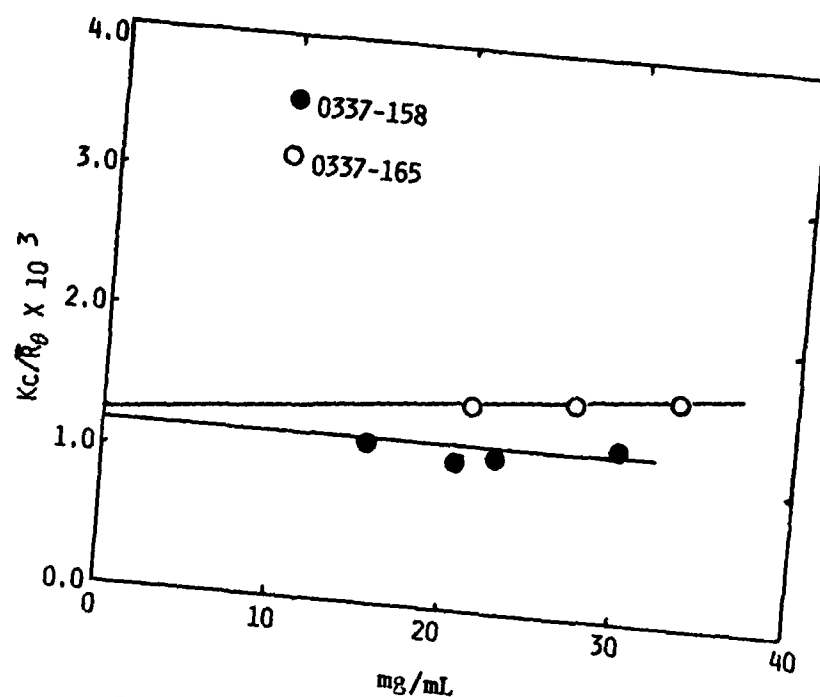


FIGURE 9. $Kc/\bar{R}_\theta$ Versus Concentration
Obtained on GAP Samples in THF.

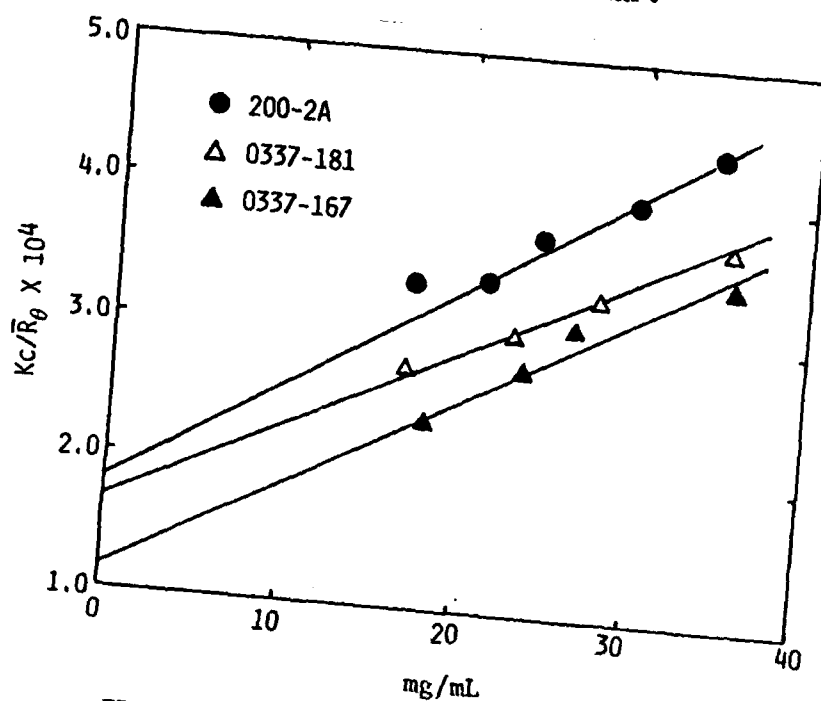


FIGURE 10. $Kc/\bar{R}_\theta$ Versus Concentration
Obtained for GAP Samples in THF.

TABLE 5. GAP and PECH $\bar{M}_w$, $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and Functionality (F).

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	F
GAP				
0337-158	1410	1130	1.25	2.08
0337-165	1020	790	1.28	1.03
0337-181	3930	3190	1.23	1.62
200-2A	3230	2470	1.31	2.00
0337-167	4590	3510	1.30	3.05
PECH				
HX101	1260	920	1.38	1.81
L9620	640	470	1.37	1.17
L9654	4610	3500	1.31	1.91
HX102P	2630	2000	1.31	1.86
LX392	3640	2450	1.48	2.3
L9621	1330	970	1.38	0.70
3mL99	6580	3960	1.66	...

In all cases, the molecular weights found were in the range expected from the equivalent weight determinations, and the molecular weight distribution increased with an increase of degree of polymerization. It is also very impressive that LALLS data can be obtained with reasonable accuracy even for the very low molecular weight species such as 0337-165 and L9620. Although LALLS studies are generally intended for high molecular weight materials, the detection of oligomers and small molecules by light scattering can be achieved from solutions at high concentration. Averaging molecular weights as determined from the fundamental LALLS equation at high solute concentration is valid as long as the second virial coefficient remains constant over that concentration range.

Also, note that the polydispersity index increases with increasing molecular weight in both GAP and PECH, and in general, is lower in the GAP series than in the PECH precursors. The removal of low molecular weight impurities occurs during the preparation of GAP from PECH, which may account for the decrease in $\bar{M}_w/\bar{M}_n$.

The functionalities of the GAP products are as predicted except for 0337-181, which shows a functionality less than two. This is consistent with the functionality of 1.86 found by gelation point (Reference 14).

Although a functionality of less than two was found through two different techniques, the actual magnitudes are in question and further experimentation, such as fractionation studies and preparative GPC, is to be done to fully characterize the functionality of their product.

Figures 11 and 12 show the GPC/LALLS responses for the low-molecular weight mono- and difunctional GAP and PECH run at 4 mg sample

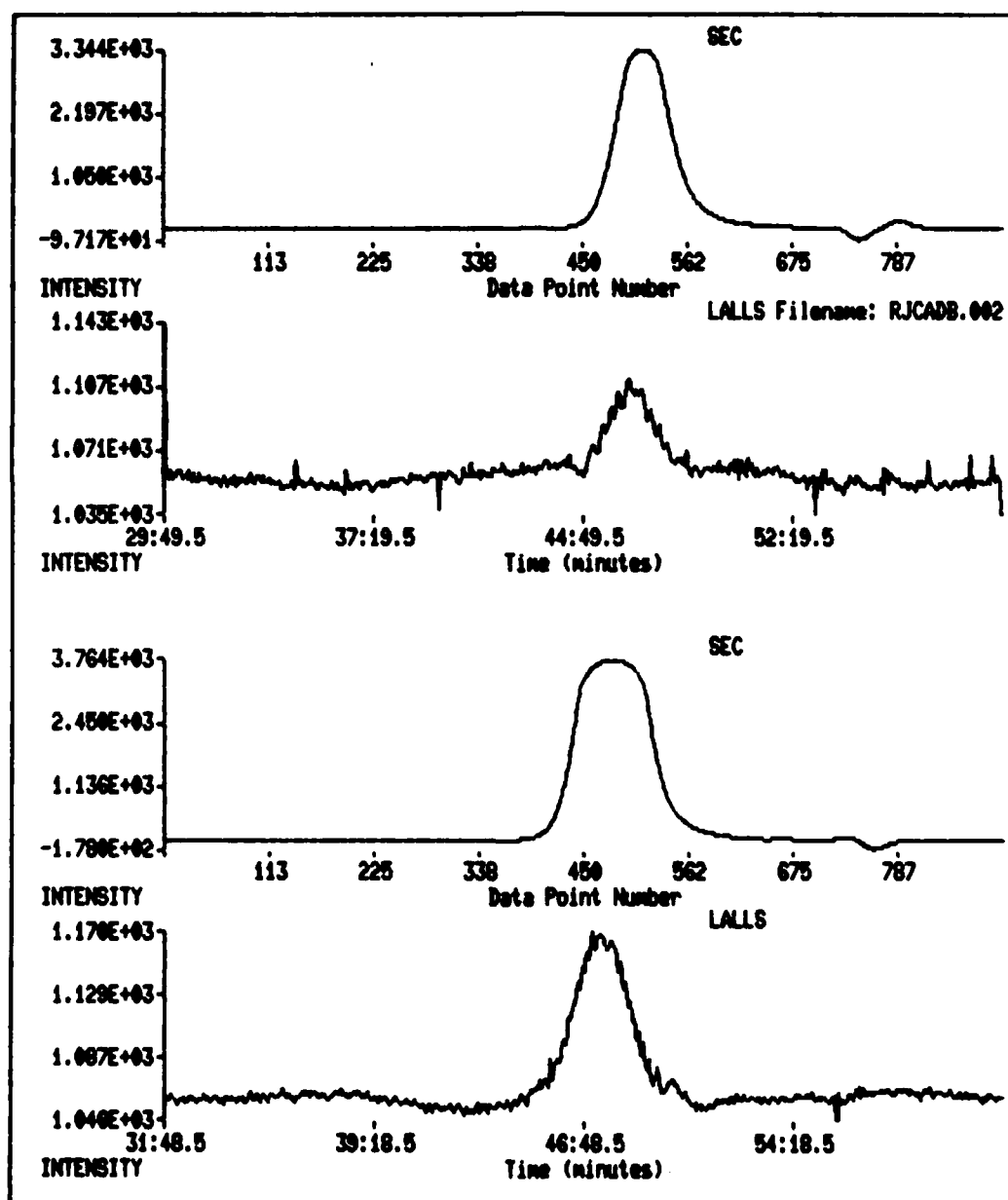


FIGURE 11. GPC/LALLS of GAP 0337-158 (Upper) and PECH HX101 (Lower).

loading. Although low-molecular weight materials of 1000 Daltons or less are generally difficult to detect by light scattering experiments, detectable and more or less gaussian curves were obtained for these samples. It is also evident in Figure 12 that the low molecular weight components were removed from the PECH L9620 during GAP 0337-165 preparation.

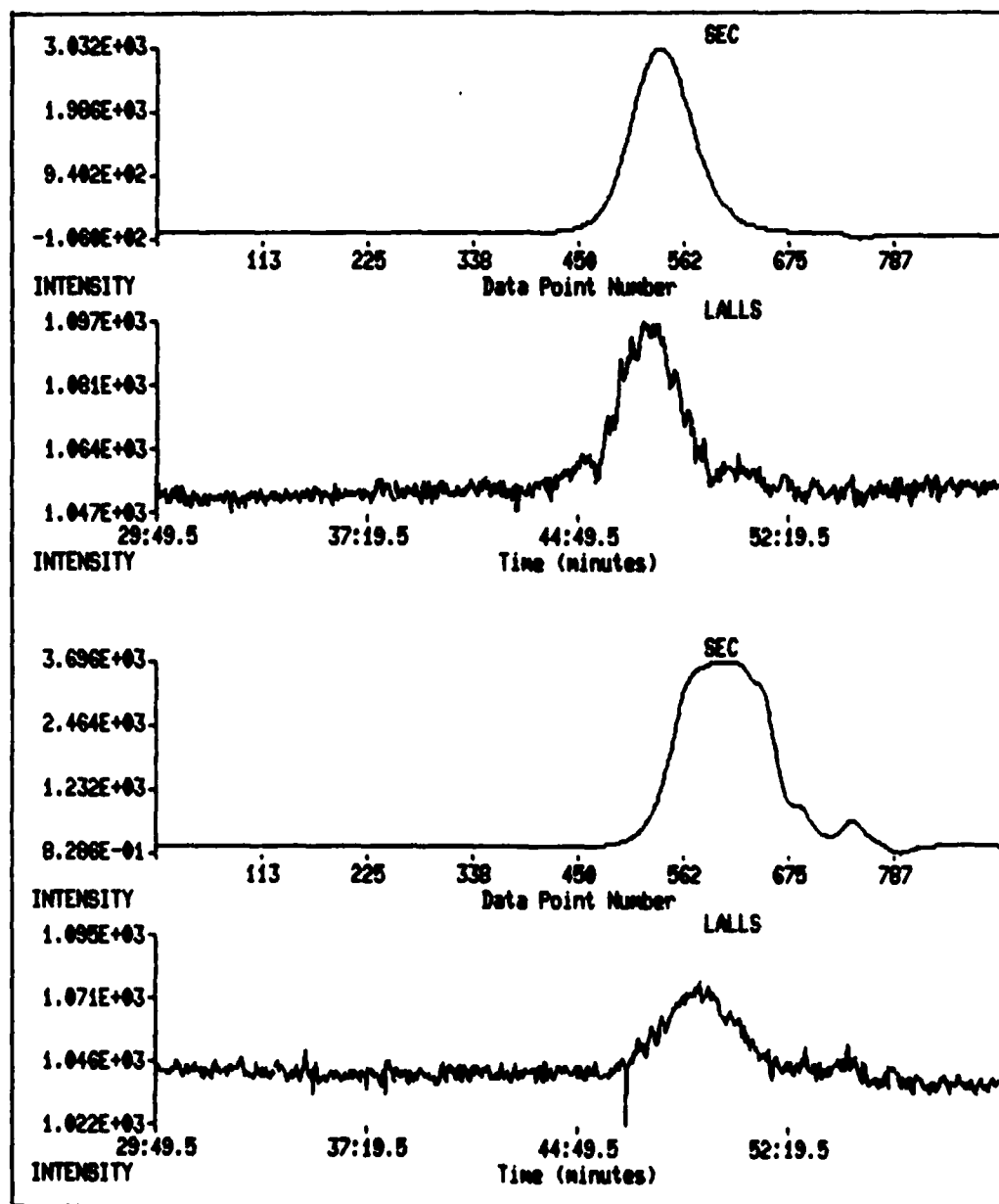


FIGURE 12. GPC/LALLS of GAP 0337-165 (Upper) and PECH L9620 (Lower).

Figure 13 shows that both GAP 0337-181 and PECH L9654 contain a low concentration of a high-molecular weight material. The molecular weight of this fraction was found to be approximately 9000 when integrated separately. Fractionation studies would be very useful in determining the differences in structure and properties of these two modes of molecular weight distributions. In Figures 14 and 15, a high molecular weight fraction was not as clearly defined; however, the curves are skewed towards the high molecular weight end.

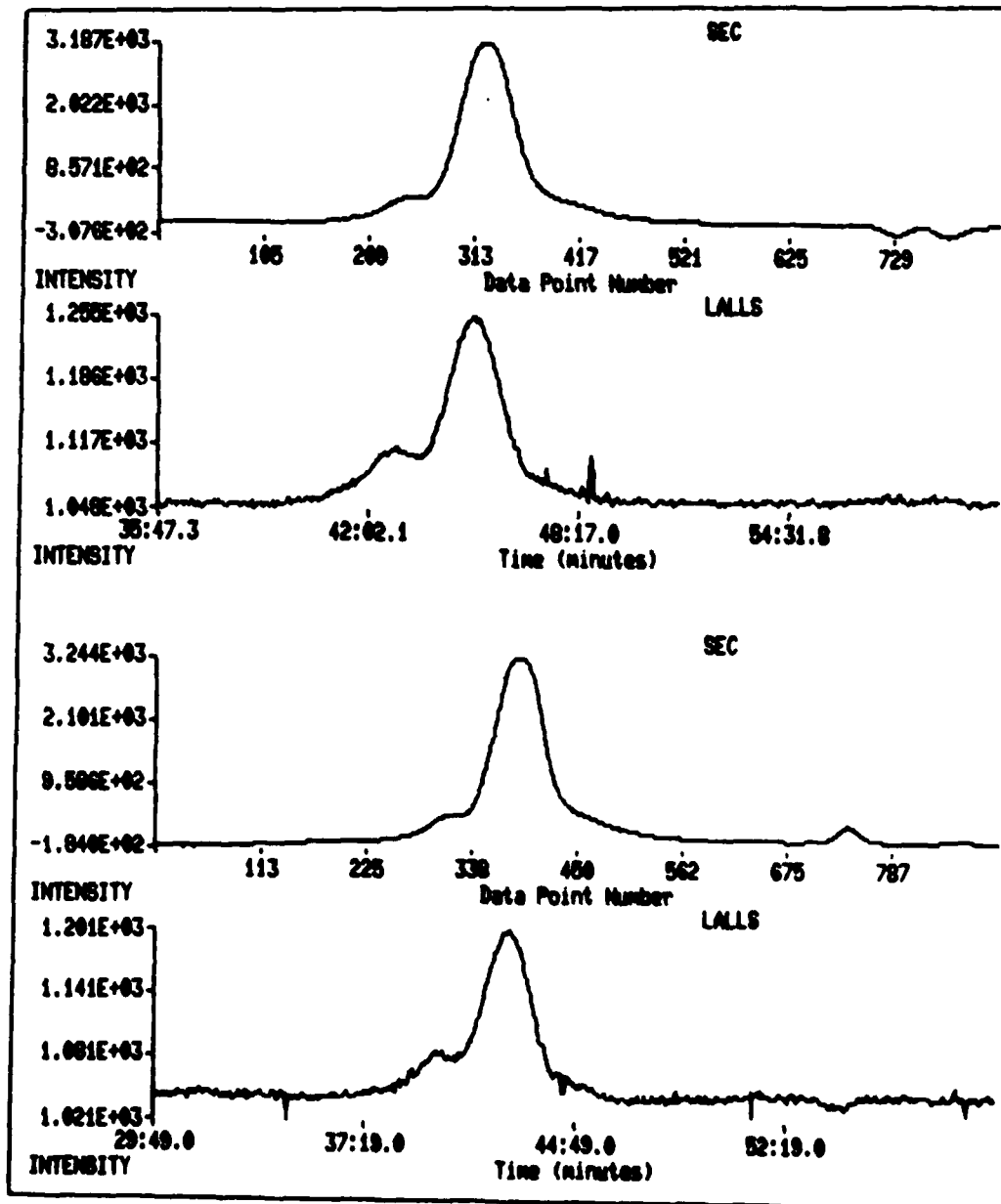


FIGURE 13. GPC/LALLS GAP 0337-181 (Upper) and PECH L9654 (Lower).

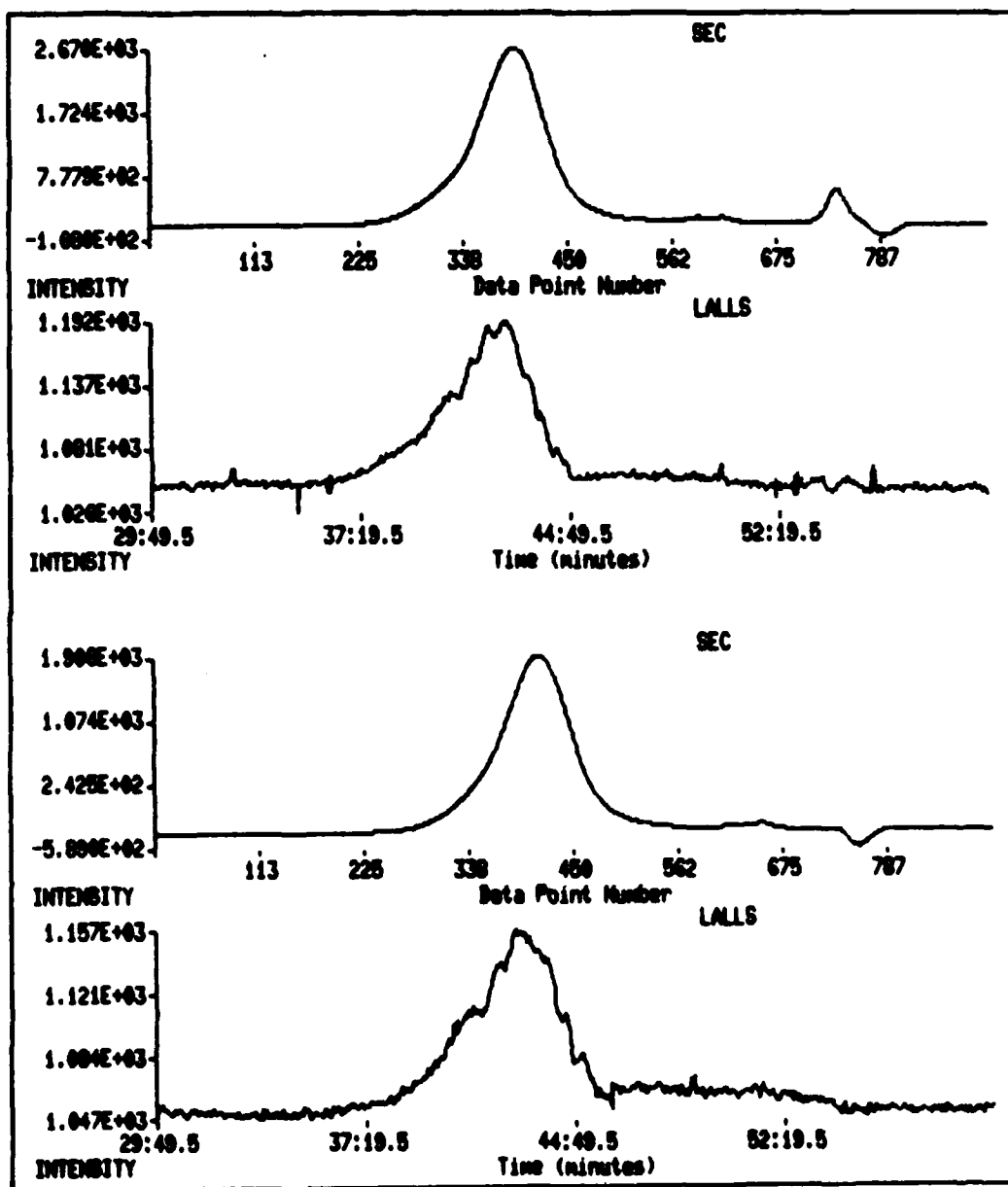


FIGURE 14. GPC/LALLS of GAP 200-2A (Upper) and HX102P (Lower).

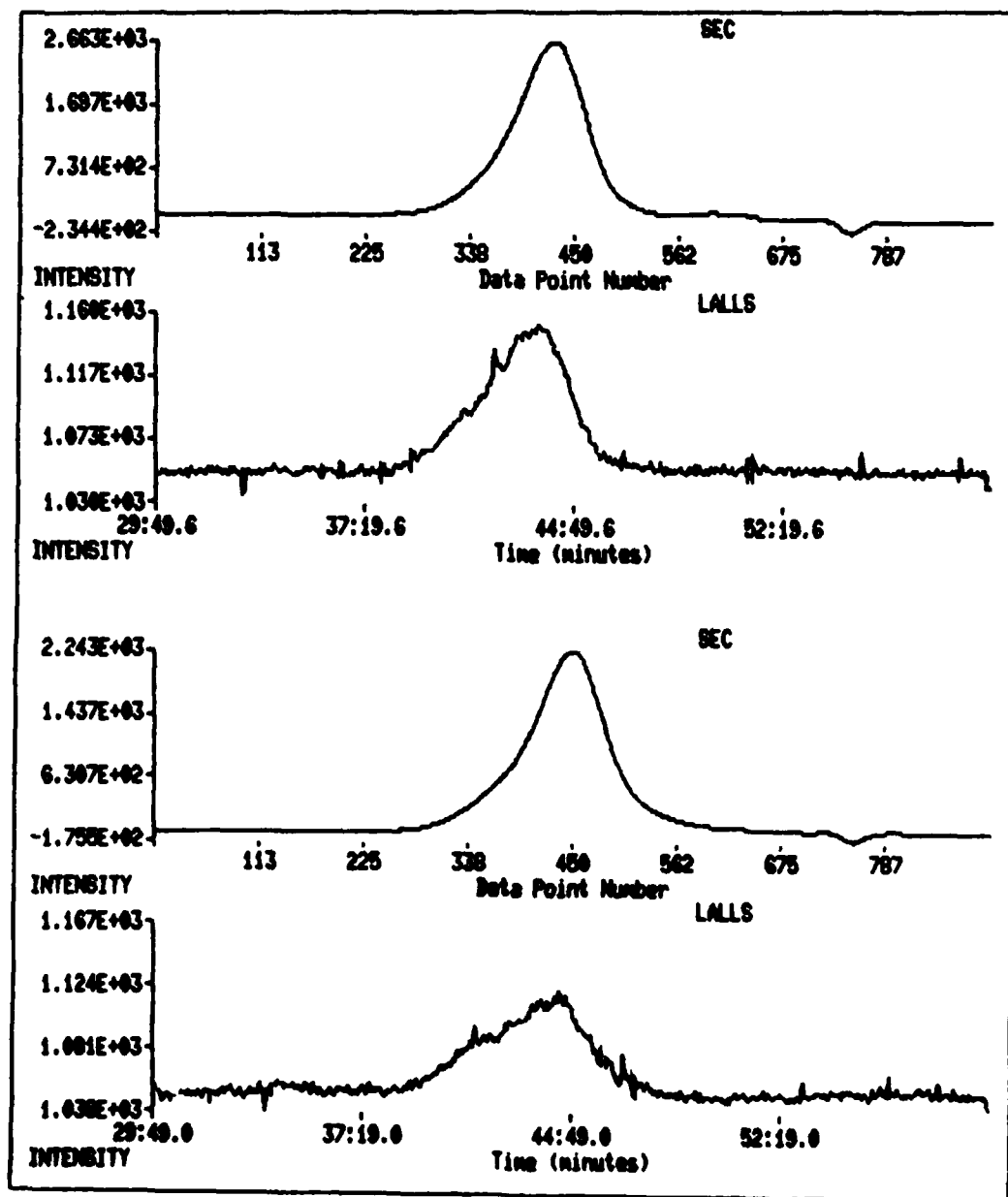


FIGURE 15. GPC/LALLS of GAP 0337-167 (Upper) and PECH LX392 (Lower).

The GPC/LALLS of PECH L9621 in Figure 16 is interesting in that the LALLS shows that the broad distribution of polymer size is a mixture of several types of polymers. Fractionation studies would be helpful in gaining information on the type of polymers present.

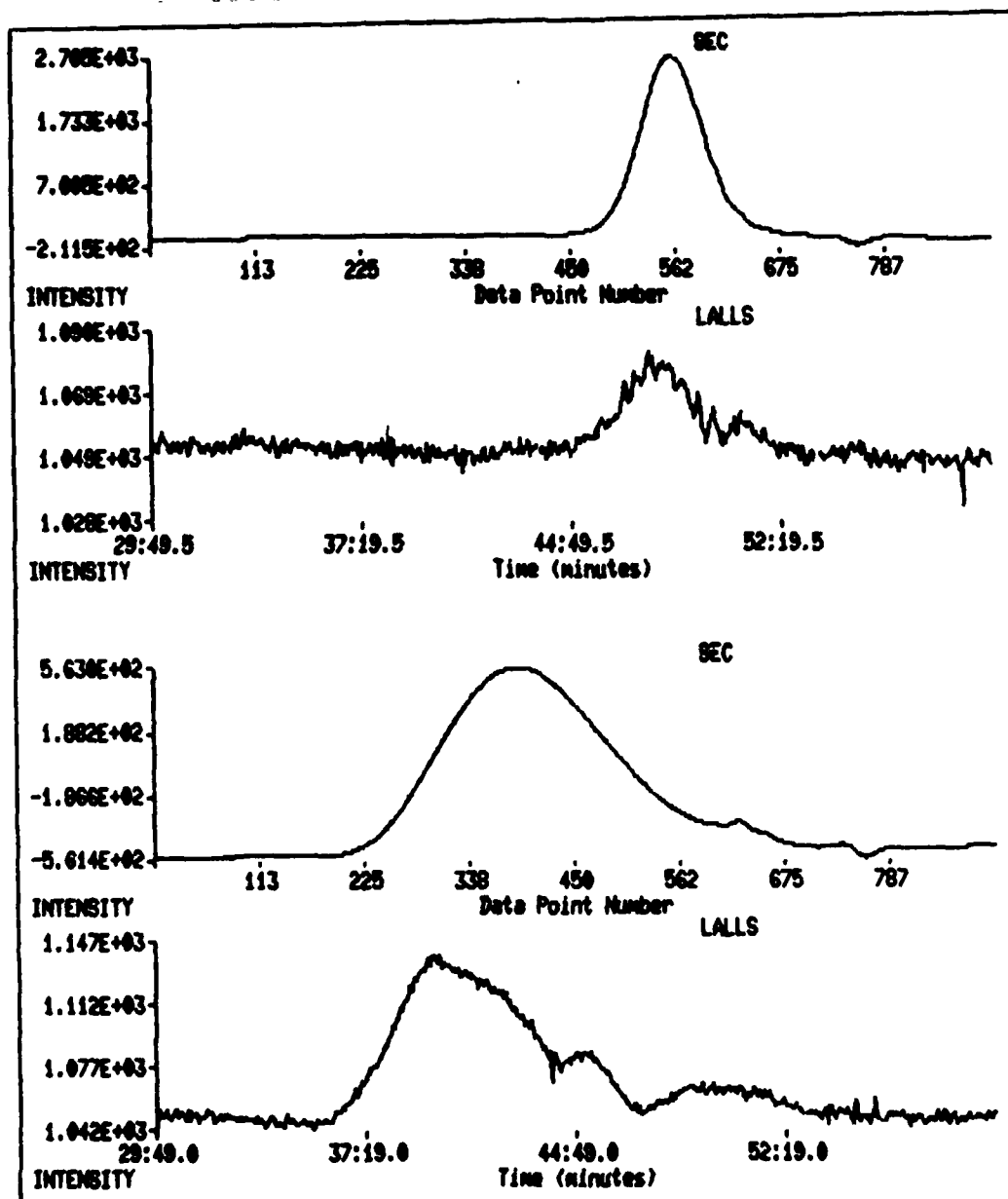


FIGURE 16. GPC/LALLS of PECH L9621 (Upper) and PECH 3M L9916 (Lower).

CONCLUSIONS

The specific refractive index, second virial coefficient, average molecular weights, and molecular weight distributions were determined for polyoxetanes, GAP, and PECH energetic polymers by using low-angle laser light scattering techniques. This method allows molecular weight determination without the use of calibration standards. In addition, useful data on low molecular weight materials was obtained for molecular weights as low as 700 when analyzed at high solute concentration. These results are valid as the second virial coefficient remained constant over the concentration range studied.

Combining LALLS and a concentration detector with GPC provides information on polymer composition, existence of branching, the presence of polymer mixtures and polymer functionality which cannot be obtained from GPC equipped with a concentration detector done where the use of calibration would lead to inaccurate results.

RECOMMENDATIONS

New energetic binders and other polymer systems should be analyzed by GPC/LALLS to accurately determine the molecular weight, molecular weight distribution, and polymer sample composition. The following method is recommended.

1. Determine the specific refractive index increment, dn/dc , of the polymer sample in a suitable solvent.
2. Calculate the polymer optical constant, K .
3. Measure the "excess" Rayleigh factor, $\bar{R}_\theta$, over a broad concentration range by static LALLS.
4. Construct a plot of $Kc/\bar{R}_\theta$ versus concentration and determine the second virial coefficient.
5. Run a sample on a GPC equipped with a refractive index and LALLS detector using the parameters determined above for molecular weight calculations.

The current system is somewhat limited in that only polymers completely soluble at room temperature may be analyzed. A number of thermoplastics and thermoplastic elastomers are dissolved with difficulty at room temperature. Furthermore, sample capacity is currently in the mg range and efforts to collect separated fractions for further evaluation would be useless.

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It is strongly recommended that the GPC/LALLS system be upgraded through the acquisition of commercially available instrumentation which would allow the chromatography of samples at higher temperatures and of larger size samples.

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