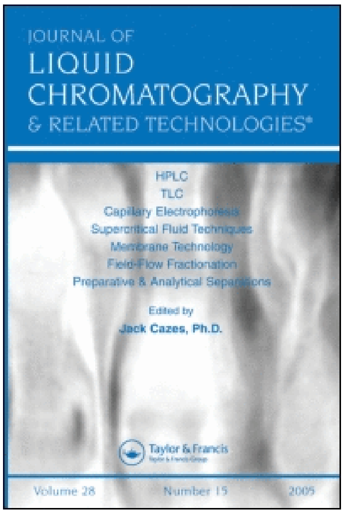

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STUDYING ABNORMAL VISCOSITY BEHAVIOR IN DILUTE OLIGOMER SOLUTIONS BY SEC AND RHEOLOGY

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ABSTRACT

We report here on the study of oligomer solutions with negative viscosities, i.e., the viscosity of the solution is less than that of the neat solvent ($\eta < \eta_s$) or the intrinsic viscosity of the solution is less than zero ($[\eta] < 0$), observed both in Poiseuille and Couette flow. These effects have been measured for several concentrations of non-functionalized styrene monomer in DMAc/0.5% LiCl at 35°C and for functionalized styrene monomer as well as for different concentrations of polyethylene oligomer in trichlorobenzene at elevated temperature. In both cases, measurements were performed as part of a size-exclusion chromatography (SEC) set-up, utilizing differential viscometers of the Wheatsone bridge type. The SEC configuration, using high-resolution oligomeric columns, permitted unambiguous determination of the degree of polymerization at which the solution viscosity changes from positive to negative in DMAc/LiCl, with static light scattering detection ruling out the possibility of an analyte clustering effect being responsible for the observed

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behavior. Ultimately, an appropriate explanation for this unusual effect was provided by steady-shear rheometry measurements of styrene-DMAc/LiCl mixtures, applying predictive rules for one-phase binary mixtures.

Key Words: Negative viscosity; Size-exclusion chromatography; Rheology; Oligomers; Polystyrene; Polyethylene

INTRODUCTION

Quantitation of low molar mass species via size-exclusion chromatography (SEC) and related techniques has become increasingly important in recent years, as the biological roles of oligosaccharides become more clearly defined[1] and the need to accurately determine the oligomeric portion of synthetic polymers has fallen under the purview of regulatory agencies.[2] Said quantitation is also a task fraught with difficulties. For a long time, columns with the necessary resolution to separate individual members of a series were non-existent. Advances in rugged, low-pore-size columns have now remedied this for both natural[3] and synthetic[4] polymers. Though band broadening issues remain,[5] once separation has been successfully effected, scientists are left with the daunting task of choosing detection methodologies with the sensitivity and accuracy needed for quantitation.

Concentration-sensitive detectors, such as refractometers and ultra-violet spectrometers, would appear ideally suited to this task, as their signal response (RI or UV) is not normally associated with molar mass. Difficulties arise in using these detectors in the oligomeric region, however, due to the fact that, at low molar masses (generally, below ~3500 Da) end-group effects result in different values of the specific refractive index increment ($\partial n/\partial c$) or of the molar absorptivity (ε) for oligomers of the same chemical species. As $\mathrm{RI} \propto (\partial n/\partial c) \times c$ and $\mathrm{UV} \propto \varepsilon \times c$ (where $c =$ solution concentration), non-constant values for ($\partial n/\partial c$) or ε result in different peak areas for the same solution concentration of oligomeric members of a homologous series. Therefore, when using these types of detectors for oligomeric analysis, either ($\partial n/\partial c$) or ε must be determined for each individual species being quantitated. These same considerations extend to the use of light scattering detectors, where the signal also depends on ($\partial n/\partial c$) or ε, with the additional hindrance that $\mathrm{LS} \propto M \times c \times ((\partial n/\partial c)^2$ or $\varepsilon^2)$, such that low molar mass (M) compounds have traditionally been considered to produce negligibly small signals at the concentrations normally used in SEC experiments. The so-called "evaporative light scattering" or "evaporative mass" detectors, in addition to not being true mass detectors (i.e., peak area is not always independent of flow rate),[6] suffer from the fact that oligomeric species are usually swept away with the bath gas used for pneumatic desolvation in these instruments.

Like light scattering photometers, viscometers are also molar mass-sensitive detectors. While the LS signal depends on the weight-average molar mass, the signal from the viscometer, which measures a colligative property, depends on the number-average molar mass. As such, $\text{VISC} \propto \text{M}^a \times \text{RI} \times (\partial n/\partial c$ or $\varepsilon)^{-1}$, with a being the exponent in the Mark–Houwink equation ($[\eta] = K\text{M}^a$, where $[\eta]$ is the intrinsic viscosity of the solution and the constants K and a are determined empirically). Viscometers are usually regarded as slightly more sensitive than light scattering detectors in the low molar mass regime though, for quantitation purposes (e.g., by means of a universal calibration curve),[7] their signal must still be combined with that from a concentration-sensitive detector, bringing about the considerations mentioned above. For a comprehensive discussion of data reduction in multidetector SEC, the reader is referred to Ref. (8).

In this paper, we explore another, rather unusual, feature that may arise in using viscometry as a detection method in SEC; that is the issue of negative viscosity changes in oligomer solutions. Specifically, this refers to the viscosity of the solution being less than that of the neat solvent ($\eta < \eta_s$), or to the intrinsic viscosity of the solution being less than zero ($[\eta] < 0$). We report evidence of negative viscosities in solutions of polyethylene oligomer and of both neat and functionalized styrene monomer, detected initially using differential viscometers of the Wheatsone bridge type and subsequently confirmed by rheological measurements. The combined effects of solvent and temperature are noted, as well as of concentration in the case of styrene. Light scattering was employed to address the possibility of molecular clusters. Ultimately, an appropriate explanation for this unusual effect was provided by steady-shear rheometry, applying predictive rules for one-phase binary mixtures.

EXPERIMENTAL

Materials

All polymers were obtained from commercial sources and were used without further purification. Polyethylenes (PE) and polystyrenes (PS) were purchased from Polymer Laboratories (Amherst, MA), styrene monomer and Santonox® from Aldrich (Milwaukee, WI), 1,2,4-trichlorobenzene (TCB), *N*,*N*′-dimethyl acetamide (DMAc), D-glucose, and LiCl from Fischer (Pittsburgh, PA).

SEC/Viscometry

For measurements in DMAc/LiCl, the salt was oven-dried overnight at 150°C and maintained in a desiccator. After dissolving 5 g of LiCl in 1 L of

DMAc at ~100°C, the solvent (DMAc/0.5% LiCl) was allowed to cool to less than 50°C and filtered through a 0.45 μm PTFE (Teflon) filter membrane (Phenomenex, Torrance, CA). Samples were prepared by shaking the solutions on a laboratory shaker for one hour at room temperature. Solution concentrations, injected volumes, and injected masses are given in Tables 1 and 2. Unfiltered solutions were injected into a system consisting of a Waters 590 programmable HPLC pump (Waters, Milford, MA), a Shodex degassing unit (the mobile phase was also degassed by He-sparging in addition to vacuum degassing), a Waters 717+ autosampler, a Viscotek H502B differential viscometer (Viscotek, Houston, TX), a DAWN EOS multi-angle light scattering photometer (Wyatt, Santa Barbara, CA), and an Optilab DSP interferometric differential refractive index detector (Wyatt). The detectors were connected in series with the refractometer last due to back pressure considerations in this detector's cell. All detectors were maintained at 35.0(±0.1)°C. Connected to this system were two OligoPore analytical SEC columns (Polymer Labs), of 6 μm particle size and 100 Å pore size. The columns were maintained at 35.0(±0.1)°C with a Waters TCM column

Table 1. Intrinsic Viscosity of Oligomer Solutions in DMAc/0.5% LiCl at 35°C

Sample	Solution Concentration (mg/mL)	Injected Volume (μL)	Injected Mass (mg)	$[\eta]_w$ (dL/g)
Styrene	49.12	400	19.65	−0.0009
	25.05	400	10.02	−0.0005
	13.18	400	5.27	−0.0003
PS 162	49.95	400	19.98	0.0034
	25.60	400	10.24	0.0017
	13.58	400	5.43	0.0009
PS 208	51.40	400	20.56	0.0095
	51.40	200	10.28	0.0046
PS 370	66.50	400	26.60	0.0172
	66.50	100	6.65	0.0042
PS 510	66.50	400	26.60	0.0211
	66.50	100	6.65	0.0052
PS 578	66.50	400	26.60	0.0264
	66.50	100	6.65	0.0064
Glucose	26.00	300	7.80	0.0607

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Table 2. Intrinsic Viscosity of Oligomer Solutions in TCB at 135°C

Sample	Solution Concentration (mg/mL)	Injected Volume (μL)	Injected Mass (mg)	$[\eta]_w$ (dL/g)
PE 170	5.00	300	1.50	−0.0020
PE 282	5.00	300	1.50	0.0036
PS 162	49.20	300	14.76	−0.0017
	25.72	300	7.72	−0.0010
PS 580	25.02	300	7.51	0.0145

temperature system. Mobile phase was DMAc/0.5% LiCl (same as solvent), at a flow rate of 1.0 mL/min.

For measurements in TCB, 6 g of Santonox (3-*tert*-butyl-4-hydroxy-5-methyl-phenyl sulfide) was dissolved in 1 L of TCB at room temperature by inversion shaking. The Santonox is added to prevent oxidative degradation of samples at high temperatures. The solvent was then filtered through a 0.2 μm nylon filter membrane (Phenomenex). 50 mg of PE was added to 10 mL of TCB/Santonox, the solutions were heated to 135–150°C, with gentle swirling, until samples appeared clear to the eye. No heating was necessary for dissolution of PS 162 or of PS 580 in TCB. Unfiltered solutions were injected into a high-temperature SEC system (Model 150C, Waters) equipped with a differential refractive index detector and retrofitted with a differential viscometer (Model 150R, Viscotek). The detectors were connected in parallel. The temperatures in the injector and column compartments were maintained at 135.0°C. Vacuum degassing of the solvent was performed with an on-line Shodex degasser. The SEC column set in this system consisted of three 20 μm Mixed A columns preceded by a guard column (Polymer Laboratories). The temperature in the pump/solvent compartment was maintained at 50.0°C. The mobile phase was TCB/1.5 mg/mL Santonox (same as solvent), at a flow rate of 1.0 mL/min. All temperatures within the 150C were controlled to within +/−0.1°C.

In both cases (DMAc/LiCl and TCB), data acquisition, calculations, and plotting were performed using a Viscotek DM 400 data manager and Viscotek's TriSEC GPC software (V. 3.0, Rev. B.01.01). All results are based on averages of at 4–6 injections from three separate dissolutions of each sample. For solutions of PE, which were several times more dilute than solutions of PS, the viscometer trace was filtered using a 13-point Savitsky–Golay algorithm *for graphical purposes only* [i.e., unfiltered data was used for $[\eta]$ calculations].

Rheology

Experiments were performed on an AR2000 rheometer (TA Instruments, New Castle, DE). An aluminum DIN concentric cylinder (Couette) geometry was used, with a 1 mm gap and cylinder height of 42 mm. All samples were run at a temperature of 35.0°C using a thermally controlled jacket around the outer cylinder (all temperatures in the rheometer are controlled to within ±0.5°C). Prior to data acquisition, the rheometer was calibrated for air bearing friction, instrument inertia, and geometry inertia. Due to the very low viscosity of the fluids measured, the air bearing was triple precision mapped. Because of the strong dependence of viscosity on temperature, a torque peak hold measurement was performed on a 20°C test specimen added to the 35.0°C geometry to determine the amount of time required to reach thermal equilibrium. There was virtually no decrease in viscosity with time, indicating excellent heat transfer. Nevertheless, the samples were allowed to equilibrate for 5 minutes before performing a 10 minute steady state shear experiment at 1 μN-m of torque, equivalent to approximately 10^{-2} Pa shear stress for these materials and this geometry.

The pure styrene monomer (Styrene) was the first sample to be run. Subsequent dilutions with DMAc/0.5% LiCl were prepared by removing a known amount of sample from the cylinder with a volumetric pipette, cleaning the pipette with acetone, and carefully drying, then back-adding an appropriate amount of DMAc/LiCl solvent to achieve the desired Styrene concentration. It must be noted, however, that twice in the sequence of samples, the geometry was completely removed from the instrument and cleaned and dried thoroughly before performing measurements on the next dilution. This cleaning was performed between replicate runs of the 50% solution due to an unusual appearance of the viscosity data, and prior to the pure DMAc/0.5% LiCl run.

RESULTS AND DISCUSSION

Classical hydrodynamic theories treat the solvent as a spatially uniform Newtonian continuum with viscosity η_s, such that incorporation of a body into this continuum will result in a solution with increased viscosity relative to that of the neat solvent.[9,10] As mentioned in the Introduction, viscosities were initially determined by means of on-line differential viscometers as part of the SEC set-up. Both the H502B and 150R models (room temperature and high temperature, respectively) are virtually identical. A schematic of the former is given in Fig. 1. As shown in the figure, this configuration is a fluid flow analog of the Wheatstone bridge electrical circuit.[11,12] The differential pressure transducer measures the change in pressure across the bridge (*DP*), while the inlet pressure transducer measures the pressure change through the bridge (*IP*). The polymer

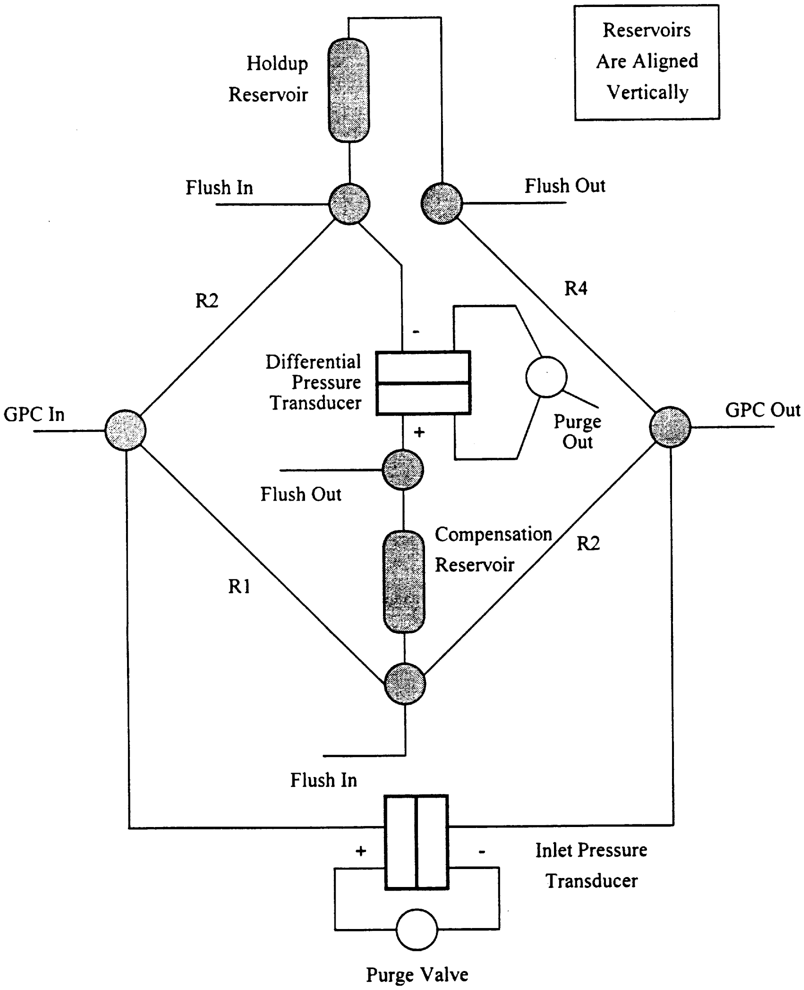

Figure 1. Schematic diagram of the Viscotek H502B differential viscometer.

solution flows through one of the capillaries while solvent flows continuously through the other three. This allows subtraction of the solvent contribution, with the *DP* signal being proportional to the specific viscosity, η_{sp}, as defined by Eqs. (1) and (2):

$$\eta_{sp} = \frac{4DP}{(IP - 2DP)} \tag{1}$$

$$\eta_{sp} = \eta_{rel} - 1 = \frac{(\eta - \eta_s)}{\eta_s} \tag{2}$$

where η is the viscosity of the solution, η_s the viscosity of the neat solvent, and η_{rel} the relative viscosity ($\eta_{rel} = \eta/\eta_s$). This type of viscometer has been found to be approximately one order of magnitude more sensitive than a conventional glass tube viscometer.[11]

Figures 2–4 show the output from the differential viscometers' differential pressure transducers (*DP*) for the samples under consideration, as well as for solvent blanks run on the same day. The solvent used for the blanks was from the same batch used to prepare the polymer solutions. These blanks serve to show the viscosity changes (positive or negative) that can be unambiguously attributed to the polymers. The negative viscosity change of the styrene monomer (Styrene, $M = 104$ Da) is observed in DMAc/LiCl at 35°C (Fig. 2). (Henceforth, when referring to the solvent, the temperature is considered an implicit parameter). A negative *DP* transducer response may be interpreted as $\eta < \eta_s$ ($s =$ DMAc/LiCl, TCB). Overlaid onto the *DP* signal for Styrene in Fig. 2 are the signals for *n*-butyl terminated styrene monomer (PS 162); for PS 370, a sample comprised of dimer, trimer, and higher oligomers of styrene; and of a DMAc/LiCl solvent blank. Two observations are evident from this Figure. Firstly, Styrene appears to exhibit non-size-exclusion behavior, eluting from the columns at approximately the same time (volume) as one of the styrene oligomers. This is likely due to interactions of the double bond of the vinyl group of Styrene with the column packing, as all other members of the series lack the alkene functionality. Secondly, it is also seen that Styrene is the only member of the series exhibiting a solution viscosity less than that of the neat solvent. The data in Table 1 show that this negative viscosity correlates to solution concentration, with the intrinsic viscosity of the styrene solutions becoming increasingly negative as a function of Styrene concentration.

Tables 1 and 2 give information about the effects of molar mass and the combined solvent/temperature effects on the intrinsic viscosity, $[\eta]$, of each sample. The latter is defined via Eq. (3), where c is the concentration of the analyte in solution:

$$[\eta] \equiv \lim_{c \to 0} \frac{\eta_{sp}}{c} \tag{3}$$

Intrinsic viscosities were calculated using a "batch intrinsic viscosity" (batch IV) approach in which only the viscometer signal is used and the solution concentration is input into the calculations manually. In other words, the refractive index detector's signal is not used. The batch IV approach was preferred over relating the concentration to the area under the refractometer curve due to the $(\partial n/\partial c)$ issues mentioned in the Introduction. Also, at the highest

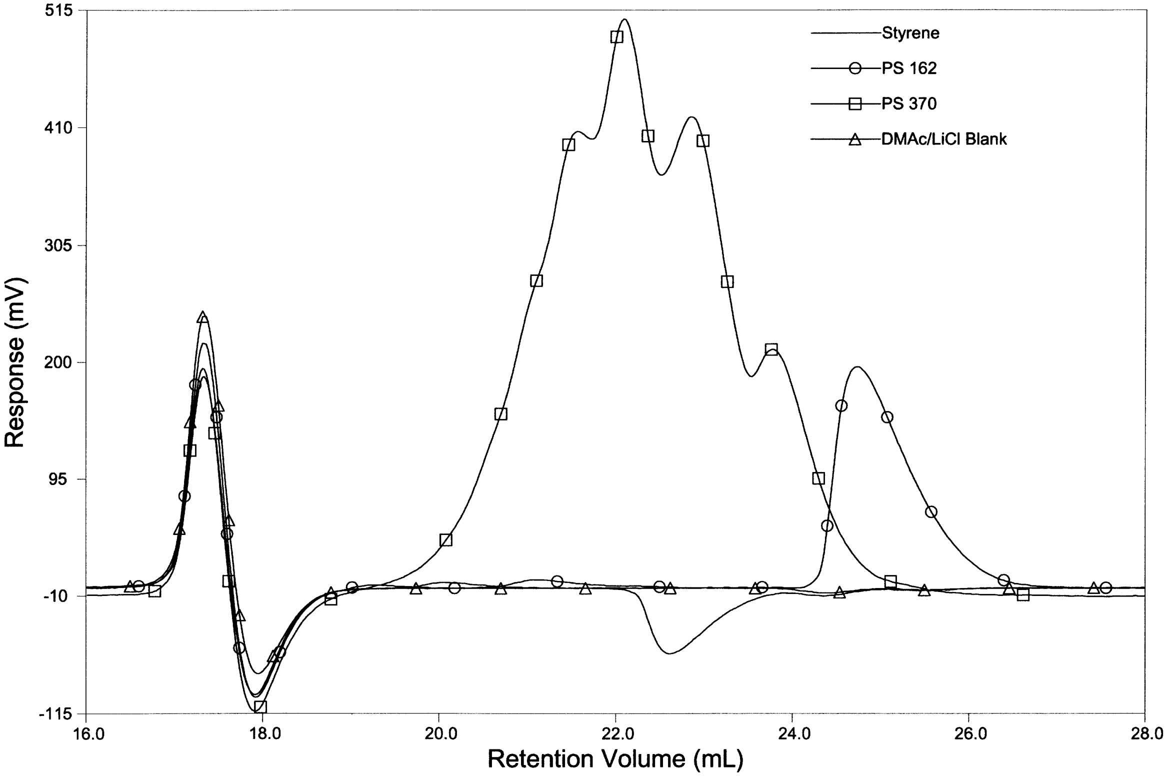

Figure 2. Viscometer differential pressure traces of Styrene, PS 162, PS 370, and solvent blank. Data obtained in DMAc/0.5% LiCl at 35°C.

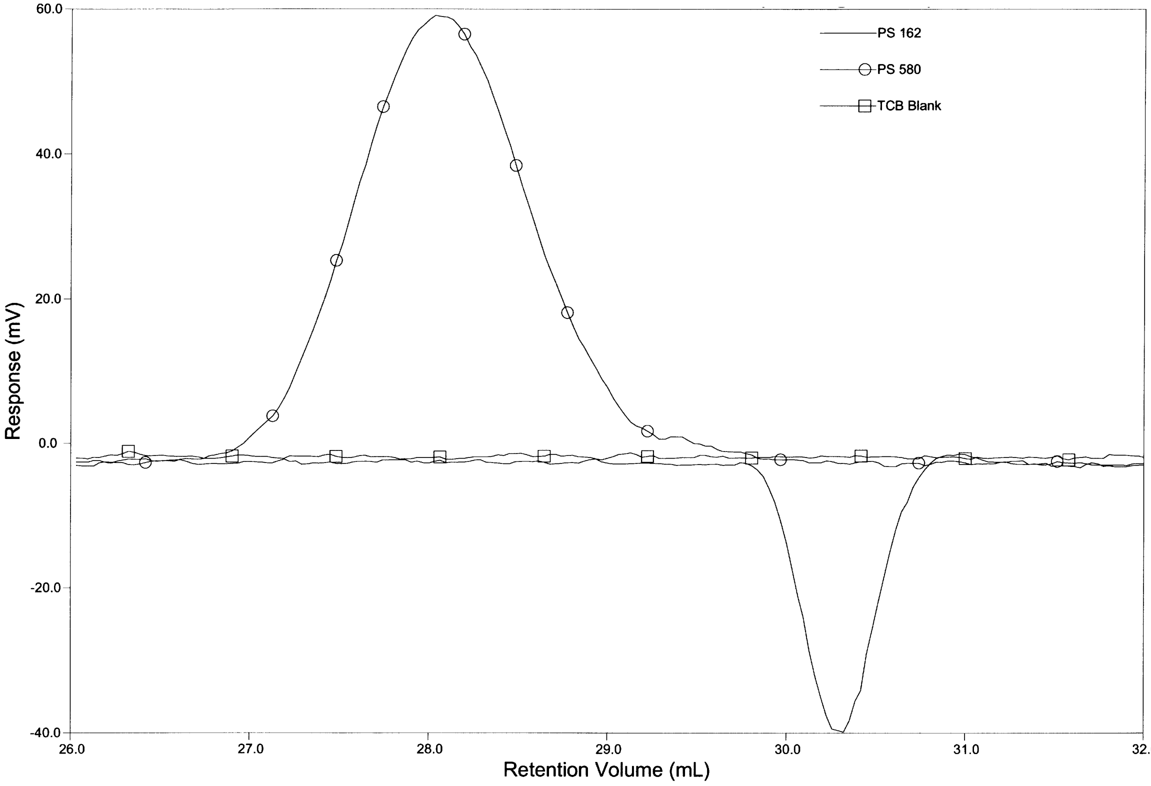

Figure 3. Viscometer differential pressure traces of PS 162, PS 580, and solvent blank. Data obtained in TCB/Santonox at 135°C.

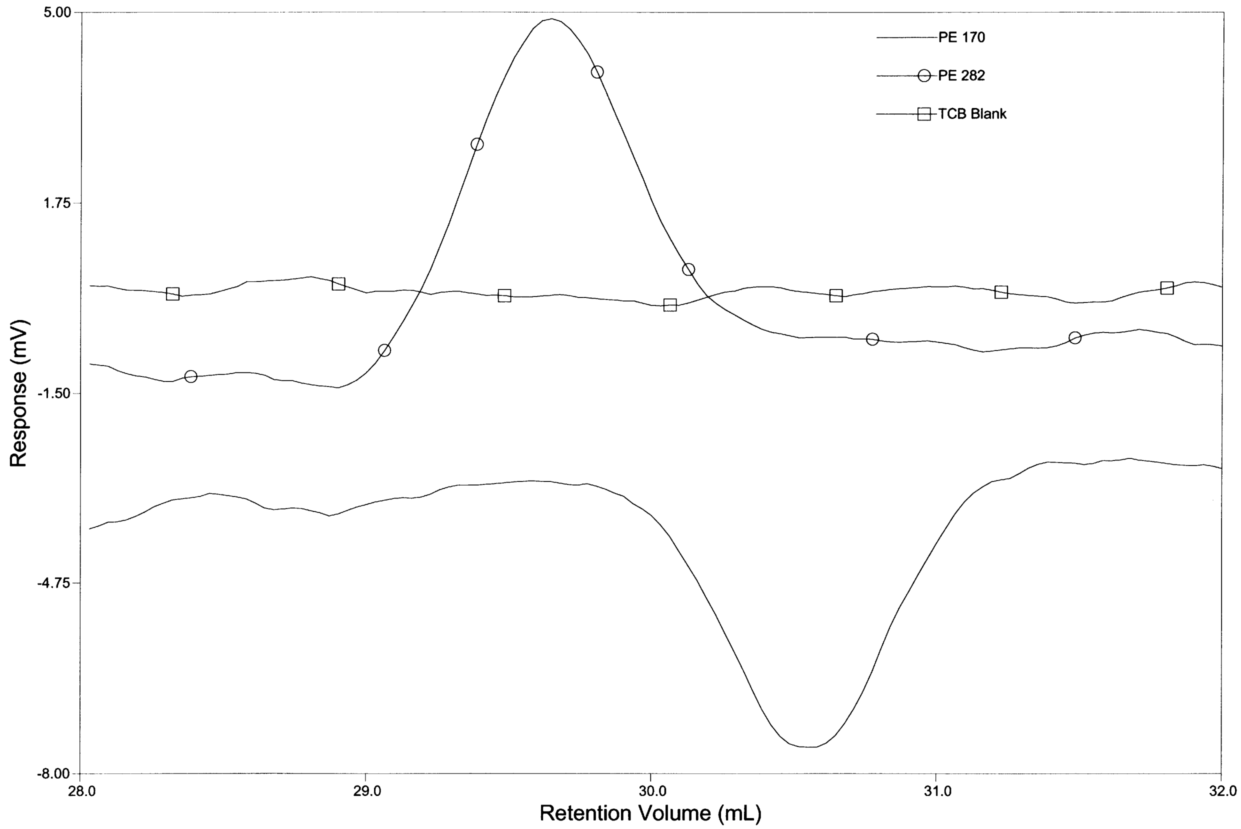

Figure 4. Viscometer differential pressure traces of PE 170, PE 282, and solvent blank. Data obtained in TCB/Santonox at 135°C.

concentrations, the refractometer signal went off-scale. The batch IV approach yields weight-average intrinsic viscosities only. The TriSEC software used for the calculations does not integrate negative *DP* peaks. In cases where $DP < 0$, the viscometer peak was inverted, the intrinsic viscosity calculated, and the sign of the resultant $[\eta]$ then changed from positive to negative. As the viscometers used here actually measure a change (increase or decrease) in pressure through and across the bridge, as outlined above (Eqs. (1) and (2)), this approach toward quantitating negative intrinsic viscosities should be valid.

Tables 1 and 2 and Figs. 2 and 3 show the combined effects of solvent and temperature on the viscosity of Styrene and styrene oligomer solutions. $[\eta]$ is negative for Styrene in DMAc/LiCl, positive for PS 162 in the same solvent, but negative for PS 162 in TCB. The effects of concentration on the negative viscosity of PS 162 in TCB are also noted in Table 2. Once again, the relationship between intrinsic viscosity and solution concentration is roughly linear for the two measurements performed. Unfortunately, instrument failure has prevented us from exploring whether the viscosity of Styrene solutions in TCB is greater or less than the viscosity of the solvent, as well as determining (using columns with higher resolution, such as those used in the DMAc/LiCl experiments) at exactly which degree of polymerization the viscosity of solutions of styrene oligomers becomes positive in TCB.

Figure 4 is the *DP* signal overlay of solutions of the polyethylene oligomers dodecane (PE 170) and octadecane (PE 282) in TCB, as well as of a TCB solvent blank. PE 170 is seen to lower the viscosity of the solution with respect to that of the solvent, while PE 282 has the opposite effect. No PE oligomers with intermediate degrees of polymerization to those reported were readily available for study. Other researchers have measured $[\eta]$ in tetrahydrofuran (THF) at 30°C for PE 170, PS 162, as well as for PE 142 (decane).[13] In all these cases $[\eta] > 0$. These determinations were done under similar conditions to those reported here, utilizing a differential viscometer (Viscotek Model 110) of essentially identical design to ours. These data provide for a particularly interesting comparison. PE 170 and PS 162 are seen to have negative intrinsic viscosities in TCB at elevated temperature, but positive intrinsic viscosities in THF at room temperature. Unfortunately, even the low molar mass PEs studied here are insoluble in DMAc/LiCl, precluding comparisons in this solvent system.

DMAc/LiCl is a useful solvent in which to conduct dissolution and derivatizations of a large number of oligo- and polysaccharides, including such difficult to dissolve biopolymers as cellulose, chitin, and starch.[14-17] As such, anhydrous D-glucose ($M = 180\,\mathrm{Da}$), a basic building block of many natural polymers, was also analyzed in this solvent. It should be mentioned that the glucose sample utilized here was likely a racemic mixture. D-glucose exists in aqueous solution as an equilibrium mixture of the diastereomeric α and β forms of the hemiacetal ring along with a small amount ($<0.5\%$) of the open-chain aldehyde.[18,19] While the mutarotation from α-D-glucose to β-D-glucose and vice-versa does not occur (or is severely retarded) in polar aprotic solvents such as dimethyl sulfoxide or DMAc, it is likely that the particular sample used here, sold simply as “D-glucose”, is a mixture of the two isomers. In any case, not only was the intrinsic viscosity of the monosaccharide positive but, as seen in Table 1, it was several times higher than that of oligostyrene solutions of higher molar mass and concentration. No results are reported in TCB, as D-glucose was found to be insoluble in this solvent.

It should be noted that both mono- and poly-disperse standards, as well as polydisperse samples of both polystyrene and polyethylene, with higher molar mass than the polymers in the tables, are routinely analyzed in our laboratory using identical experimental setups to those outlined here (i.e., same detectors and same solvent/temperature conditions).[17,20] Results have always been consistent with expectations ($[\eta] > 0$) and are not included here as they do not add to the discussion of negative viscosity.

It should also be noted that the phenomenon of negative viscosity is by no means new. It was elegantly explored by Lodge et al. for solutions of polybutadiene in Aroclor 1248, at high frequency conditions, using oscillatory electric birefringence,[21,22] and by Yang and Wang for polybutadienes in oligomeric ($M_n = 1.0$ and 1.5 KDa) butadienes, using oscillatory shear and differential scanning calorimetry.[23] The negative viscosity effect has also been observed in magnetic fluids.[24,25] While certainly interesting, all of these experiments are far removed from those presented here, either due to the frequency, viscoelastic, or electromagnetic regions being explored. More apposite to the present discussion is the work of Yamakawa et al. Using specially designed Ubbelohde-type viscometers, these authors showed that oligoisobutylenes (oIB) with molar mass of 112 Da and 168 Da possessed a negative $[\eta]$ in isoamyl isovalerate at θ conditions (25°C). However, of the two, only the 112 Da oIB was found to have $[\eta] < 0$ in benzene at θ conditions (25°C).[26] These authors also found that $[\eta] < 0$ for a polyisobutylene (PIB) dimer in benzene at 25°C (θ) (27), and for oligo(dimethylsiloxane) dimer through pentamer in bromocyclohexane at 29.5°C (θ).[28] A “draining effect” was postulated by which a liquid structure of some kind in the solvent is destroyed by molecules of solute when the former is in the vicinity of the latter.

How then to explain the results presented here? Are molecular clusters responsible? These constructs, sometimes referred to as “vitrons”, have been invoked by various authors, including Minnick and Schrag to explain the decrease in both viscosity and birefringence of Aroclor solvents upon addition of oligomers of butadiene and isoprene.[22,29] Using the light scattering detector, we can show that this is not the case for Styrene in DMAc/LiCl. Figure 5 is an overlay of the signals from the viscometer *DP* transducer and from the 90° photodiode of the MALS unit for Styrene. Correlating exactly with the negative *DP* peak is a single

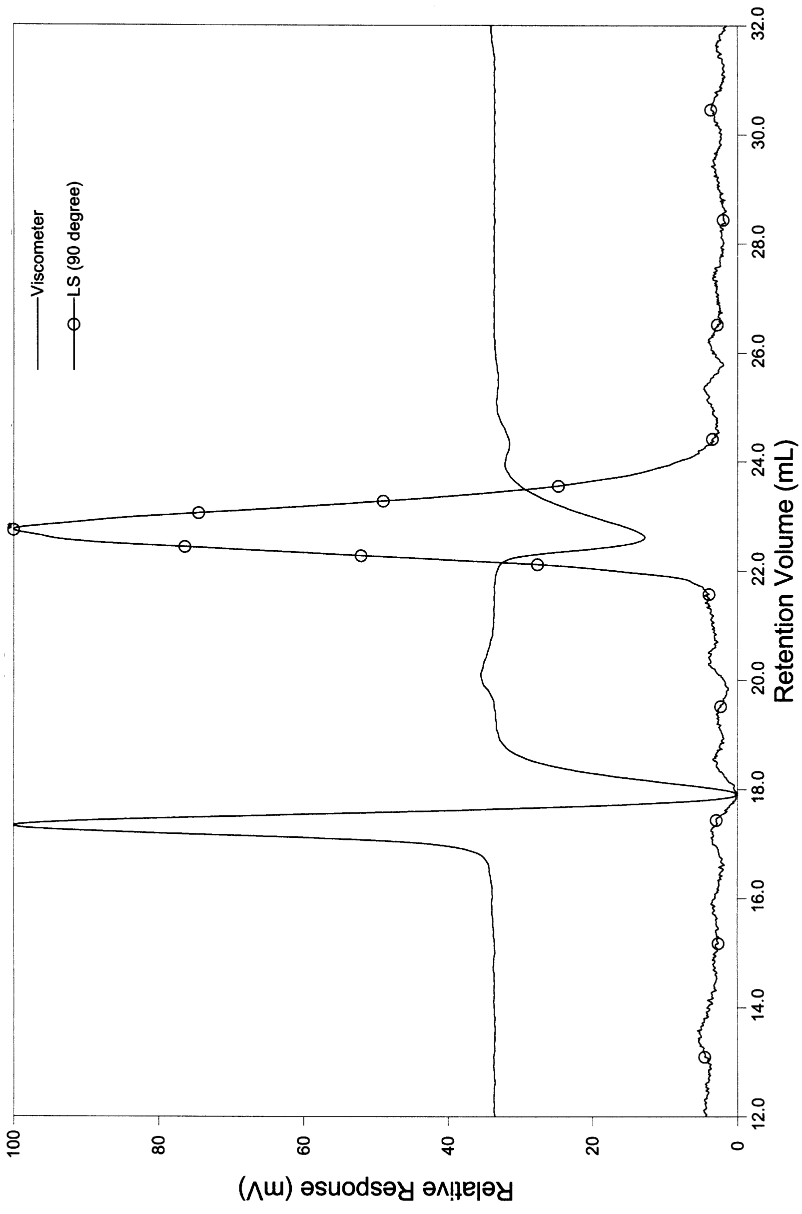

Figure 5. Viscometer differential pressure trace overlaid upon light scattering detector (90° photodiode) signal for Styrene in DMAc/0.5% LiCl at 35°C.

(positive!) peak from the light scattering photometer. Styrene clusters, which would have a higher molar mass than the unaggregated analyte, would certainly be observed by LS, where the signal is directly proportional to M (vide supra). Either 100% of the analyte is clustering, which is highly unlikely, or else clusters are not the answer. Interestingly, while the injected mass necessary to obtain this LS signal was quite high (~ 20 mg), even injecting 5 mg of Styrene yielded an LS peak with acceptable signal-to-noise ratio ($S/N > 10$). Recent reports have extended the use of LS detection to the oligomeric region for polystyrene.[30] The present work attests to the fact that light scattering detection can now extend fully through the oligomeric region to the point of a single, monomeric repeat unit.

Literature values of room temperature (20°C) viscosities indicate that the viscosity of styrene (0.76 mPa-s) is lower than that of neat DMAc (0.97 ± 0.05 mPa-s) but higher than that of THF (0.52 ± 0.03 mPa-s). The room temperature (25°C) viscosity of dodecane (1.35 mPa-s) is also higher than that of THF at the same temperature (0.46 mPa-s).[31,32] It thus appears possible and even likely that the negative viscosity effect observed in our SEC/viscometry experiments is due to a mixing effect of solutes with lower viscosities than the solvents. Under the very reasonable assumption that we are dealing with two completely miscible Newtonian fluids, and that the resulting mixture is also Newtonian in the region of applied shear stress being probed, we have employed steady shear rheometry to study the viscosity of solutions of Styrene in DMAc/0.5% LiCl at 35°C, the same temperature as in our SEC experiments using this solvent. Results from the rheology experiments are given in Fig. 6, which plots the viscosity of the Styrene-DMAc/LiCl solutions vs. the volume fraction of Styrene. It becomes immediately evident that upon addition of Styrene to the solvent the viscosity of the solution becomes lower than that of the solvent, and is so over the entire range of the abscissa, becoming increasingly negative as more Styrene is added.

The question then becomes, can this behavior be quantitatively explained? To this effect we have applied the predictive rules for mixtures, specifically the rule for one-phase binary mixtures,[33] Eq. (4):

$$\eta = \eta_A \phi_A + \eta_B \phi_B + P \phi_A \phi_B \tag{4}$$

where η is the viscosity of the solution, η_A and η_B are the viscosities of the two individual components (Styrene and DMAc/LiCl, respectively), and ϕ_A and ϕ_B are the volume fractions of the two components in the mixture. The P term corresponds to an interaction term, which can be positive or negative depending on the system. Thus the last term on the right-hand side of the equation represents the concentration-dependent interaction between two different chemical species. From the data in Fig. 6 we calculate $P = 0.129$ mPa-s.

The solid line in Fig. 6 represents the least squares fit of the data for styrene in DMAc/0.5% LiCl, at 35°C, modeled using Eq. (4). The prediction from the

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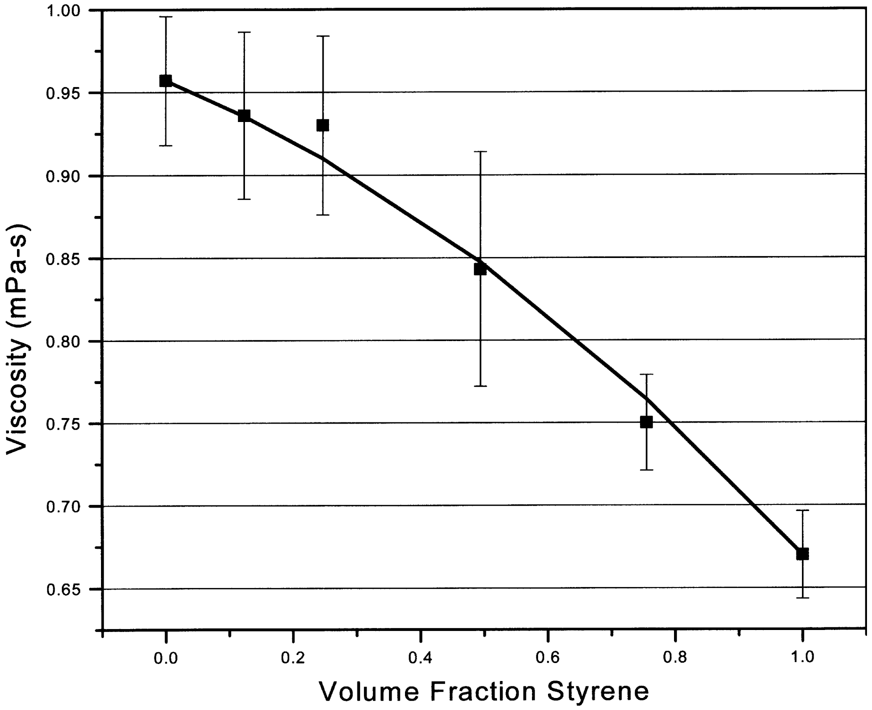

Figure 6. Viscosity of Styrene-DMAc/0.5% LiCl solutions vs. volume fraction of Styrene. Data obtained using Couette geometry at 35°C. Solid line represents prediction from Eq. (4).

rule of mixtures shows excellent correlation with the experimental data ($r^2 = 0.992$), such that we feel justified in ascribing the seemingly abnormal behavior of the monomer and oligomer solutions to fundamental hydrodynamic properties of matter and not to other, more esoteric effects.

CONCLUSIONS

We have detailed the determination of negative intrinsic viscosities of monomer and oligomer solutions, namely of styrene monomer in DMAc/0.5% LiCl at 35°C and of PS 162 and PE 170 in TCB at 135°C, using differential viscometers of the Wheatstone bridge type. The differential viscometer was found to possess the sensitivity necessary for measuring the negative viscosities at both elevated and room temperature and in different solvent systems, over a range of concentrations.

The negative viscosity effect was confirmed rheologically by steady shear measurements of solutions of Styrene and DMAc/LiCl at the same temperature as the SEC experiments. The effect was therefore shown to manifest itself both under Poiseuille (Wheatsone bridge viscometer) and Couette (concentric cylinder rheometer geometry) conditions of flow. Furthermore, applying predictive rules for one-phase binary mixtures it was found that the rheology data was in excellent agreement with physicochemical hydrodynamic expectations. There is no need to invoke mechanisms such as “draining effects” or “vitrons” to explain the data presented here. Moreover, the existence of solute clusters was effectively disproven by the use of static light scattering, which was shown to have the appropriate sensitivity to detect monomeric styrene with excellent signal-to-noise ratios.

It was also shown that D-glucose, the building block of the most abundant biopolymers, possessed a positive viscosity in DMAc/LiCl, a preferred solvent for the characterization of difficult to dissolve polysaccharides.

SAFETY CONSIDERATIONS

N,*N*′-dimethyl acetamide is an exceptional contact hazard that may be harmful if inhaled or absorbed through the skin and may be fatal to embryonic life in pregnant females. (Baker Chemical Co., *N*,*N*-dimethylacetamide, Material Safety Data Sheet, 1985, D5784-01).

1,2,4-trichlorobenzene may cause irritation to the respiratory tract, skin, eyes, and liver damage. (Burdick & Jackson, 1,2,4-trichlorobenzene, Material Safety Data Sheet).

Styrene monomer may be harmful if swallowed, inhaled, or absorbed through the skin. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Exposure can cause skin irritation and may alter genetic material. (Aldrich Chemical, Styrene, Material Safety Data Sheet).

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