

# News



The Society of Plastics Engineers

ENGINEERING PROPERTIES  
& STRUCTURE DIVISION

November 2007



EPSDIV is pleased to reprint the Best Paper Award for ANTEC 2006. Seen left to right are: EPSDIV President Brian Grady; EPSDIV Board member Sadhan C. Jana; and two of the paper's authors Dr. Ashish M. Sukhadia, Research Fellow, Chevron Phillips Chemical Company LP; and Dr. David C. Rohlfing, Research Fellow, Chevron Phillips Chemical Company LP. The entire paper, *Observations and Insights Into Some Unusual Rheological Behavior of Metallocene Catalyst Polyethylene Resins*, is found on pages 6-14.

## ANTEC 2008

You are NO LONGER required to submit an abstract for ANTEC 2008. Simply submit your paper online by December 3. See page 2 for more ANTEC changes.

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## EPSDIV Plans for the Future



**Brian Grady serves as EPSDIV  
Chairperson for 2007-08**

In this President's message, I want to talk about EPSDIV's technical program plans for the future.

### ANTEC

Historically, EPSDIV's focus has been at ANTEC; EPSDIV is consistently the division that has the largest number of papers presented at ANTEC. SPE has introduced a new two-track system for papers, "commercial" and "technical" (for more information, see the *Write Now* brochure which can be found at [www.4spe.org/conf/](http://www.4spe.org/conf/)).

It is up to you, the author, to designate your paper one way or another and it will be interesting to see how many EPSDIV papers choose each track. I am sure our Technical Program Chairs, **Murali Rajagoplan**

and **Pierre Moulinie** will be happy to help if you have questions.

I want to make it clear that "commercial" does NOT mean "industrial", all papers presented in the past in EPSDIV would definitely qualify as "technical". The biggest differences are that materials, procedures etc. can be much less well-defined in a commercial paper, trade names etc. can be used extensively in commercial papers, and the work does not have to be new.

The idea behind this change was to encourage papers that otherwise would not have qualified for presentation at ANTEC. However, a paper that still would have qualified for ANTECs in the past might fit better in the "commercial" section, don't hesitate to designate your paper if you think this way.

We at EPSDIV would like to see many more submissions to EPSDIV because of this addition. You might be thinking, "well, this message is a bit late, since the abstract deadline is past". However, another change this year is that you are NOT required to submit an abstract before the deadline, as long as your paper is submitted online by **December 3**, you are fine.

Our plan is to grow our ANTEC program by encouraging more industrial researchers to present papers be-

cause of this new designation.

### TOPCON

As I stated in my last message, EPSDIV is planning a TopCon in 2008. The location will be in the Philadelphia area and the date is tentatively scheduled for October; the exact dates have not yet been decided. The title of the conference will be *New Approaches in Polymer Characterization: Nanocomposites, Block Copolymers and other Nanostructured Materials*.

All of us at EPSDIV look forward to seeing you at this conference; more details will follow in future newsletters.

—Brian Grady

**There is a NEW two-track system  
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## SPE Expanding Technical Focus



Don Witenhafer

Highlights of the Fall Council meeting are as follows:

- A budget was passed, with a dues increase from \$118 to \$125. Other than the dues increase, the other interesting item is the fact that *Plastics Engineering* is losing money, and very likely there will be six online and six print issues in 2009 (in 2008, we will do twelve print issues). The reason for the delay is primarily technological

(the concern about the website being able to handle a high quality publication) but there is also a concern about whether advertisers can be retained.

- An important new benefit to SPE members will be free electronic access to SPE Journals (Polymer Engineering and Science, Polymer Composites etc.).
- We are losing about 2-3% members per year over the last two years. SPE membership is around 19,000 currently. There is a concern that the dues increase will cause us to lose more members than the 2-3%.

SPE is rapidly expanding our technical focus. Three special interest groups (a precursor to divisions) were approved: Bioplastics, Plastics in Building and Construction, and Medical Plastics Europe.

Overall, there was positive support

for ANTEC being held at the McCormick Center with NPE in 2009. However, at this point, it is possible that co-location in 2009 will not happen because of hotel commitments in San Antonio (where ANTEC 2009 is currently scheduled to be held).

At this point, the idea of regionalization (i.e. some strategic planning to guide grouping of small sections into larger ones either from a programming perspective or a governance perspective) seems to be dead. We have decided to let sections combine naturally (or fold naturally). Several sections were moved to provisional or abandoned status.

Currently, the International Committee has responsibility for growing SPE internationally. There are some internal issues with this framework: should the focus be changed from international to global strategic growth? What will happen exactly is not clear. There does seem to be a large chance there will be an ANTEC style meeting in Europe in the Fall of 2009.

We continue to actively recruit speakers for the SPE speakers list. You may now apply on line at the SPE web site.

— Don Witenhafer, Councilor

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## ANTEC 2008 Technical Program Chair Report

**Presenters and authors are already thinking about ANTEC 2008!**



Seen left to right, Pierre Moulinie and Murali Rajagoplan are co-chairs of the Technical Program for ANTEC 2008. For more information on these sessions contact Pierre at [pierre.moulinie@bayerbms.com](mailto:pierre.moulinie@bayerbms.com) or Murali at [Murali\\_Rajagopalan@AcushnetGolf.com](mailto:Murali_Rajagopalan@AcushnetGolf.com)

To date, EPSDIV has received 59 Abstract submissions. More are expected as paper submissions without prior abstracts are possible.

Three keynote speakers have already kindly accepted to give keynote presentations. At least two more are expected to be confirmed.

As well, Composites, Alloys and Blends and Thermoplastic Materials and Foams have indicated interest in joint sessions with EPSDIV.

### WRITE NOW!

The deadline for Paper Submission is December 3rd at 5pm.

Tools to help put together a paper for ANTEC 2008 are available at: <http://mc.manuscriptcentral.com/antec2008>

### TOPICS

EPSDIV's sessions will cover the following topics:

- Recent Developments in Polyolefins
  - Structure and Property Relationships in Engineering Resins and Blends
  - Polymer Nanocomposites
  - Films and Packaging
  - Fracture Mechanics of Polymers
  - Tissue Engineering Polymers
  - Materials for Biological Applications
  - Polymers Useful in Alternate Energy Sources
  - Smart Materials
  - Nanotechnology in Electronic and Biological Devices
  - Renewable Resources in Engineering Polymers
- See you in Milwaukee!!!

**Deadline for Papers  
December 3 at 5:00 pm.  
(No abstract submission is necessary)**



*Let's meet in  
Milwaukee Wisconsin!*

**Attend ANTEC  
2008 for the  
Plastic Encounter  
May 4-8, 2008**

Register online and attend ANTEC 2008. Two plenary speakers have been announced:

- Ed Barlow, President, Creating the Future, Inc., will speak on: A Journey Through the 21st Century
- William F. Banholzer, Corporate Vice President and Chief Technology Officer, The Dow Chemical Company, examines Challenges and Opportunities in Future Feedstocks for the Plastics Industry

Log on and register at: [www.4spe.org/conf/antec08/](http://www.4spe.org/conf/antec08/)

### Send me some news!



John Trent, EPSDIV newsletter editor, encourages members to submit articles or news for publication in upcoming issues.

## ANNUAL FINANCIAL REPORT: JULY 1, 2005 TO JULY 2006

**STARTING BALANCE as of July 1, 2006**

**\$32668.37**



*Emmett Crawford is the EPSDIV  
Treasurer for 2007/2008*

<b>INCOME</b>	<b>Actual</b>	<b>Budget</b>	<b>Variance</b>
Interest	1214.87	800.00	414.87
TOPCON Receipts	8233.95	000.00	8233.95
Newsletter Ads/Sponsorships	2500.00	5500.00	(3000.00)
Scholarship Contributions	1000.00	1000.00	0.00
SPE Rebate	5295.52	6000.00	(704.48)
ANTEC Sponsorships	6500.00	6500.00	0.00
Refund from Meeting (Hyatt)	44.42	0.00	44.42
<b>Total Income</b>	<b>24788.76</b>	<b>19800.00</b>	<b>4988.76</b>
<b>EXPENSES</b>			
General Office Expenses	0.00	100.00	(100.00)
Teleconferences	387.13	1000.00	(612.87)
Board Meetings	258.80	1000.00	(741.20)
TOPCON	6114.62	10000.00	(3885.38)
Newsletter Printing/Mailing	1070.00	1750.00	(680.00)
Awards	3260.48	4500.00	(239.52)
Scholarships/Grants	1000.00	1000.00	0.00
TPC	2835.00	4000.00	(1165.00)
Councilor Travel	1365.21	1500.00	(134.79)
BOD Travel	574.62	2000.00	(1425.38)
Student Travel Fund	500.00	500.00	0.00
Membership	0.00	300.00	(300.00)
Receptions	470.00	1000.00	(530.00)
Bank Fees	7.50	0.00	7.50
<b>Total Expense</b>	<b>17843.36</b>	<b>29650.00</b>	<b>(10806.64)</b>
<b>ENDING Balance</b>	<b>39613.77</b>	<b>22818.37</b>	<b>16295.40</b>
<b>Allocation of Funds</b>			
Checking Account		\$10743.97	
Investments		\$28869.80	
<b>TOTAL</b>		<b>\$39379.72</b>	

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## OBSERVATIONS AND INSIGHTS INTO SOME UNUSUAL RHEOLOGICAL BEHAVIOR OF METALLOCENE CATALYST POLYETHYLENE RESINS

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### Abstract

The dynamic shear rheological behavior of polyethylene resins made using a single metallocene catalyst was measured and analyzed. We observed some unusual rheological behavior that, at first glance, was more reminiscent of the well-known behavior of highly filled systems. Specifically, the viscosity exhibited yield stress-like character with a sharp upturn in the low-frequency viscosity. The standard molecular weight distribution profile for these resins was generally unremarkable. The causes of this viscosity behavior were explored by further characterization of the molecular architecture and attributed to the presence of long chain branching selectively present in the highest molecular weight fractions of the polymers.

### Introduction

In the early days of the metallocene “revolution”, metallocene catalyst technology was highly touted for its ability to generate polymers of very controlled molecular architecture. Metallocene catalysts were then, perhaps naively, thought to produce “simple” resins with very uniform chain architecture viz. a narrow molecular weight distribution (MWD), homogeneous short chain branching distribution (SCBD), equivalent composition, chain branching and chain length across the MWD and otherwise supposedly well-understood molecular structures [1-5]. The ensuing years of global research, development and commercialization activity with metallocene catalysts have shown, in fact, that those early thoughts and expectations have not completely borne out. Rather, what has happened is that the metallocene catalyst technologies have resulted in a surprisingly wide array of polymer architectures being synthesized and characterized with oftentimes unexpected or poorly understood molecular architectures and corresponding rheological behaviors [6-20].

In this paper, we report on some unusual, and not commonly reported on, rheological behavior observed in polyethylene resins made using a single metallocene (“single-site”) catalyst. Drawing upon some published literature, we attempt to provide insight into the origin of the observed behavior and further attempt to provide some bounds for when such behavior may or may not be

expected for both linear and long chain branched polymers.

### Experimental

#### Resin Synthesis

The experimental polyethylene resins L1-L4 were prepared in a Phillips type slurry-loop pilot plant, having a nominal production capacity rate of about 12 kg/hr under steady state polymerization conditions. L1-L3 were made using two catalysts together during the polymerization, while L4 was made using a single catalyst. Experimental resins A-E were made in a semi-batch, bench-scale reactor using only a single metallocene catalyst with varying levels of a proprietary co-agent as explained further in the text. For both sets of samples, the polymer fluff (flake) was subsequently extruded off-line into pellets using appropriate levels of stabilizer antioxidants. All characterization data shown was performed on the pellet samples only.

#### Absolute Molecular Weight via Light Scattering

SEC-MALS couples size exclusion chromatography (SEC) with multi-angle light scattering detector (MALS). A DAWN EOS 18-angle light scattering photometer (MALS, Wyatt Technology) was attached to a Waters 150-CV GPC system through a hot solution transfer line thermally controlled at the same temperature as the SEC columns and its differential refractive index (DRI) detector (135 °C). At a flow rate of 0.7 mL/min, the mobile phase, 1,2,4-trichlorobenzene (TCB), was eluted through two 7.5 mm X 300 mm PL 20 µm Mixed A columns (Polymer Labs) also maintained at 135 °C. PE solutions with concentrations of 1.0-1.2 mg/mL, were prepared at 150 °C for 3-4 hr before being transferred to SEC injection vials sitting in the carousel at 135 °C. In addition to a concentration chromatogram, seventeen light scattering chromatograms at different scattering angles were acquired for each injection using Wyatt's Astra® software. At each chromatographic slice, both the absolute molecular weight ( $M$ ) and radius of gyration ( $R_g$ ) were obtained. The linear PE control employed in this study was a high density broad MWD PE (Chevron Phillips Chemical Co.). The weight average molecular weight ( $M_w$ ), number average molecular weight

*Continued on next page*



( $M_n$ ),  $z$  - average molecular weight ( $M_z$ ) and molecular weight distribution ( $M_w/M_n$ ) were computed from this data.

## Results, Analysis and Discussion

We begin by first looking at a couple of data sets that we hope will serve as useful controls for this study and subsequent analysis. In Figure 1, the complex viscosity versus frequency data (Fig. 1a) and GPC traces (Fig. 1b) are shown for four resins L1 through L4. A closer examination of Fig. 1a shows that the viscosity behavior of resins L1, L2 and L3 is non-monotonic. Specifically, and particularly for resin L3, it is seen that the viscosity at low frequencies does not appear to show the typical approach to a Newtonian plateau region, as clearly observed for resin L4, but rather actually shows evidence of a sharp upturn in the viscosity. This type of viscosity behavior is mildly reminiscent of that observed in highly filled systems and associated with the presence of a yield stress [see Figure 11-4 of ref. 21]. We will refer to these non-monotonic viscosity-frequency curves as "S-shaped". Resins L1 and L2 also appear to exhibit behavior similar to L3, but to a lesser degree.

In the absence of the GPC data, this viscosity behavior might appear surprising. However, with the GPC data shown in Fig. 1b, it is seen that resins L1, L2 and L3 all have distinct high molecular weight "tails" which is absent in resin L4. The GPC data in Fig. 1b is shown more quantitatively in Table 1 through tabulation of select molecular weight average and distribution data for these four resins. Specific attention is drawn to the  $z$ -average molecular weight ( $M_z$ ), ( $M_z/M_w$ ) ratio and the weight fraction of the polymer having  $M_w$  in the molecular weight range of 1E-1E7 g/mol and 1E7-1E8 g/mol. Resins L1, L2 and L3 all have very high  $M_z$  and particularly  $M_z/M_w$  ratio compared to resin L4. Furthermore, it is clear that resins L1-L3 contain about 3 wt % (for L1 and L2) to 4 wt % (for L3) of polymer in excess of 1E6 g/mol in comparison to a negligibly small fraction for resin L4. Resins L1-L3 may thus be considered to be "blends" of two separate components, the lower  $M_w$  primary component and then the high  $M_w$  ("tail") fraction as the second component. By that definition, resin L4 is absent the second component altogether.

Resins L1-L4 were made using catalysts that are known to produce essentially linear (no significant long chain branching (LCB)) polymers. In order to understand how polymers similar to L1-L3 might generate the non-monotonic rheology behavior, several simulated blend calculations were performed.

The space constraints here do not allow for detailed elaboration of our procedures. However, it is probably useful to provide at least this general scheme that was followed in this phase of the work. The blend

simulations were limited to two-component systems. Starting with the assumptions that each polymer component was linear (no LCB) and had a log-normal Gaussian molecular weight distribution, we varied the  $M_w$  of each component, the polydispersity (MWD) of each component as well as the composition ratio of the two components to arrive at various synthetic polymer (blend) GPC profiles. The viscosity of each component was determined separately by first estimating the zero shear viscosity (using  $\eta_0 = 5.8E-14(M_w)^{3.41}$  [22] for the assumed  $M_w$  of each component, using a fixed value ( $=3.24E5$ ) of the ratio of zero shear viscosity ( $\eta_0$ ) to characteristic relaxation time ( $\tau$ ) to determine  $\tau$  and assuming a rheological breadth parameter,  $a$ , which was varied depending on the MWD. The  $\eta_0/\tau$  ratio and  $a$  parameter were both chosen based on experimental data for many linear polymers of different MWD that we have characterized over the years. The three rheological parameters viz.  $\eta_0$ ,  $\tau$ , and  $a$  were then used with a modified form of the Carreau-Yasuda [23] empirical model (assuming  $n=0.1818$ ) to determine the viscosity profile of each component from which the viscosity of the simulated blend was calculated using the Schuch blend rule [24]. While admittedly not very robust, this approach allowed us a first pass estimate of the expected rheology based on the synthetic MWD. Far more sophisticated and state-of-the-art modeling approaches may be found in other recent works [28, 29, 30].

Using the approach above to do numerous simulations, we have determined that linear polyethylene resins can only exhibit the S-shaped viscosity-frequency profile under very specific conditions that must be met simultaneously. Specifically, we have found that the S-shaped viscosity curves are only observable when the following conditions are met simultaneously:

- The polymer is a blend of at least two distinct components [A single, log-normal, Gaussian linear polymer component will always exhibit a monotonically decreasing viscosity curve, a reflection of the continuous relaxation time distribution.]
- The two components exhibit a sufficient degree of  $M_w$  separation as seen in the GPC [If the two components are not well separated in  $M_w$ , the overlap of the two relaxation time distributions precludes non-monotonic behavior.]
- The blend composition ratio is such that the high  $M_w$  fraction is significantly smaller ( $< 10$ -15 wt %) compared to the lower  $M_w$  fraction [If this condition is not met, the relaxation time distribution of the high  $M_w$  overshadows the lower  $M_w$  component, again precluding a non-monotonic viscosity profile.]

The above observations are typified in the simulation results shown in Figure 2 and Table 2 for three test cases as explained further in the figure caption. These results show that (only) when the high  $M_w$  fraction is

present as a minority component is there any indication of a “S-shaped” rheology curve.

Before we go further, we’d like to point to some (perhaps indirect) support of our findings and conclusions above in the earlier work of Trinkle and Friedrich [15]. In their work on the utility of the so-called Van Gurp-Palmen or VGP (phase angle vs. complex shear modulus) plots, the authors too noted that in the case of linear polymers (i) increasing polydispersity or MWD at fixed  $M_w$  did not introduce any inflections or change the overall shape of the VGP behavior, (ii) blends of linear low and high  $M_w$  polymer components did generate inflections or minima in the VGP plots, and further that increasing polydispersity or MWD of the two components caused these inflections to diminish and eventually disappear. This latter behavior was attributed to the lack of dominance of one distinct species on the terminal relaxation process of the polymer. These findings are in good agreement with our observations presented above.

Having established what types of linear polyethylene resins can give rise to these non-monotonic “S-shaped” viscosity curves, we now turn our attention to some more experimental resins.

The GPC and viscosity data for five experimental resins labeled A-E are shown in Figure 3a and 3b, respectively. These five resins were made using a particular, single metallocene catalyst and varying co-agent levels. The control sample A had no co-agent present while the samples B through E were made with increasing levels of the co-agent.

The GPC data in Fig. 3a, however, surprisingly shows no evidence of any higher molecular weight tails or species. This is supported by the GPC data for these samples tabulated in Table 3. It should be noted that for this particular set of samples, extreme care was taken during the GPC test to ensure that baseline selection was done carefully so that any high  $M_w$  fraction was accounted for. This GPC test was also repeated with identical results. Therefore, we are comfortable stating that these five samples contained no high  $M_w$  tails or shoulders in the conventional GPC.

In light of the earlier results and discussion with respect to the behavior seen with linear polyethylene resins, however, the rheology behavior seen in Fig. 3b, in conjunction with the associated GPC data in Fig. 3a is unexpected. That is, absent any signatures of a high  $M_w$  fraction in any of the five resins, the “S-shaped” behavior seen with samples C, D and E, in particular must have a different origin.

To understand the rheology behavior observed in Fig. 3b further, we conducted SEC-MALS experiments using the protocol described in the experimental section.

The SEC-MALS results for resins A-E are shown in Figure 4a-4e, respectively. Sample A shows essentially no detectable LCB. However, samples B-E all show clearly detectable levels of LCB that furthermore increases in LCB content progressively from sample B to E. While there are some limitations to the SEC-MALS method in terms of the ability to detect LCB at low  $M_w$ , we have been able to readily discern, through other independent studies, LCB at  $M_w$  greater than 100,000 g/mol and higher. Given that, we also conclude from the data in Fig. 4 that for samples B-E, the LCB is preferentially present only in the high  $M_w$  fraction of the polymer viz. at  $M_w$  values above 300,000 g/mol. Furthermore, it is of interest to note that for all samples B-E, the LCB level increases with increasing  $M_w$ , going from about 0.06 LCB/1000 C to 0.09 to 0.12 to 0.18 for samples B through E, respectively.

It is clear from the SEC-MALS data above that resins B-E could be considered as PE blends of a linear, low- $M_w$  component and a long chain branched high- $M_w$  component. The relative weight fraction of the two is hard to assess but, judging from the GPC-LCB distributions in Fig. 5, it would appear that the long chain branched fraction only constitutes less than about 15-20 wt % of the total polymer.

We attribute the origin of the viscosity behavior seen in Figs. 4b-4d to the superposition of two widely dissimilar relaxation time distributions of the two “components” that make up these polymers as discussed above. The linear, low- $M_w$  component is responsible for the high frequency (short relaxation time) behavior while the long chain branched, high- $M_w$  component is responsible for the low frequency (long relaxation time) behavior. Superposed, the two together give rise to the observed “S-shaped” viscosity behavior observed in Fig. 4b. We view our data and interpret our results in a fashion very similar to the observations of Moan et al.[25], who also observed unusual rheological viscosity profiles in their work on immiscible blends and attributed that to the presence of two distinct plateau regions at low and high frequencies [see Fig. 15 of ref. 25 in particular].

In fact, our work here appears to be a good confirmation of the findings of Wood-Adams et al. [14], who used the difference between a standard experimental GPC MWD profile and a “viscosity MWD” profile to assess the level of LCB in a given polymer. The “viscosity MWD” was obtained by converting experimental complex viscosity data to MWD, assuming that the polymer was linear. That is, for a polymer with LCB, the “viscosity MWD” could be interpreted as the MWD of a linear polymer that had the same complex viscosity curve as the branched polymer. For a polymer that actually contained LCB, this rheology-to-MWD conversion resulted in the prediction of a MWD profile that was typically broader and exhibited two peaks. The primary peak was a little



lower  $M_w$  and the secondary peak a little higher  $M_w$  when compared to the GPC of a completely linear polymer with the same complex viscosity curve. A re-examination of our data in Figs. 3b and 3a (branched polymers) with that in Figs. 1b and 1a (linear polymers) illustrates these points very well.

Similar findings, suggestive of two distinct relaxations, and modeled using a linear-LCB blend approach, have also been reported by Robertson et al. [20]. They observed the presence of two separate relaxations corresponding to the low and high frequency regimes, which also had very different values of the flow activation energy,  $E_a$ .

We return now to further re-examine some of our experimental data reported here. The type and extent of "S-shaped" viscosity behavior observed in Fig. 3b does not, to the best of our knowledge, appear to be widely reported on in the literature, although the linear-long chain branched "pseudo-blend" type behavior from metallocene catalyzed resins, in general, has been reported on previously as mentioned earlier. In some recent publications, it was noted that the rheology of certain metallocene catalyzed PE resins containing LCB exhibited physical gel-like behavior due to the fact that a plateau region in the plot of phase angle,  $\delta$ , versus frequency could be readily observed [20, 26]. This plateau region was postulated to be a consequence of the presence of two distinct, but partially overlapping, terminal relaxation processes [20]. Our results here, particularly as seen from Fig. 3d, show no such plateau region in the analogous VGP plot but rather what appears to a distinct intermediate maximum in the VGP representation. Yet, the polymers going from sample B to E show clearly, and increasingly, pseudo physical gel-like character. Fig. 3c shows that for samples C, D and E in particular, the storage modulus appears to become less and less frequency dependent below about 5 rad/s indicating increasing gel-like or solid-like behavior [27].

## Conclusions

In the course of our metallocene research efforts, we have encountered several instances now where the rheology of polymers, produced even with a single catalyst, exhibit some unusual rheological behavior that, at first glance, was more reminiscent of the well-known behavior of highly filled systems. Specifically, the viscosity exhibits an *apparent yield stress-like* character with a sharp upturn in the low-frequency dynamic viscosity. Yet, the standard molecular weight distribution profile for these resins was generally unremarkable.

Analysis of the effects of MWD on rheology in conjunction with additional characterization of some experimental resins via SEC-MALS revealed that the

observed rheology was a direct consequence of the presence of LCB preferentially in the high  $M_w$  fraction of the polymer. Furthermore, this fraction was estimated to be less than 20 % by weight of the whole polymer. The presence of a linear polymer (with low relaxation times) in conjunction with a minor fraction of a LCB polymer (with very high relaxation times) appears to provide the right characteristics such that when the relaxation time spectra of these two "components" overlap in the typical experimental frequency window, a non-monotonic viscosity profile is obtained.

In contrast to some recent literature, we did not observe a plateau region in the phase angle versus frequency plot. Rather, a distinct maximum was observed which became better defined as LCB increased. The reason for the different observations between our results and some of the earlier referenced work is not completely known. However, it is likely that the differences are due to the particulars of the polymers investigated with respect to their molecular, rheological and LCB characteristics. These differences, it is believed, lead to different relaxation time distributions of the "two" (linear and LCB species) components, with consequent differences in how they overlap in the typically observed (and experimentally accessible) frequency window of 0.01 – 100 rad/s. Our results therefore point to the complexity of dealing with and understanding the rheology of LCB polymers, in general, and provide reasons for some caution against making generalized conclusions as much has yet to be learnt about the details of LCB architecture and their effects on rheology. Finally, it is worth a note that metallocene catalysts, generally best known for their "single-site" character, can and have produced some complex polymer architectures, even with a single catalyst as in our study here, that in our mind raises questions about the validity of the label "single-site" catalyst.

## References

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### Keywords

**rheology, metallocene, long chain branching, SEC-MALS**

**Table 1. Molecular weight data for experimental resins L1, L2, L3 and L4.**

RESIN	$M_w$	$M_n$	$M_z$	$M_w/M_n$	$M_z/M_w$	Weight % polymer between 1E6-1E7 g/mol	Weight % polymer between 1E7-1E8 g/mol
	(kg/mol)	(kg/mol)	(kg/mol)			(%)	(%)
L1	245.41	32.88	7607.77	7.463	31.000	2.98	0.47
L2	180.74	33.41	4371.53	5.411	24.187	2.40	0.22
L3	248.59	29.30	3845.58	8.484	15.470	3.79	0.24
L4	103.87	44.19	213.49	2.35	2.0553	0.03	0.00

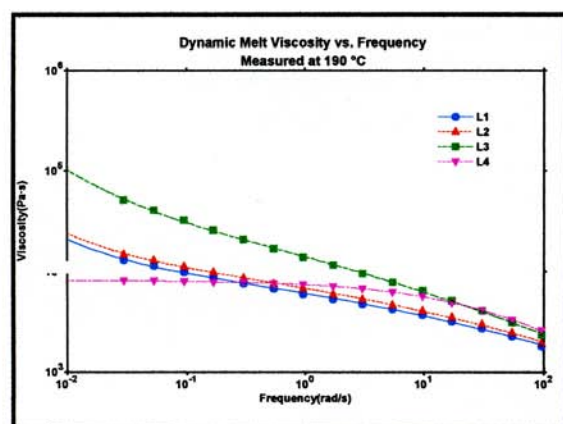
**Table 2. Molecular weight data for simulated polymers shown in Figure 2. Note the similarities between Fig. 2, case 3 and resin L3 in Fig. 1 and also the similarity between the GPC data for case 3 in this table and resin L3 in Table 1.**

RESIN	$M_w$	$M_n$	$M_z$	$M_w/M_n$	$M_z/M_w$
	(kg/mol)	(kg/mol)	(kg/mol)		
Case 1	100.00	26.32	380.00	3.80	3.80
Case 2	2089.01	256.00	6694.93	8.16	3.20
Case 3	249.71	28.22	4356.38	8.85	17.45

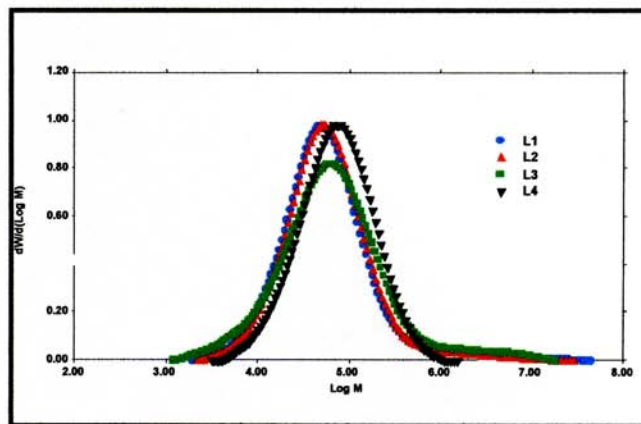
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**Table 3. Molecular weight data for experimental resins A through E. All the resins were made using a single metallocene catalyst with varying amounts of a co-agent.**

RESIN	Co-agent Level	$M_w$	$M_n$	$M_z$	$M_w/M_n$	$M_z/M_w$
	(ppm)	(kg/mol)	(kg/mol)	(kg/mol)		
A	0	103.13	32.2	259.2	3.20	2.51
B	0.5	80.03	24.6	238.3	3.25	2.98
C	1.0	66.02	21.5	191.4	3.06	2.90
D	1.5	98.56	29.5	297.7	3.34	3.02
E	2.0	65.63	20.7	189.2	3.16	2.88



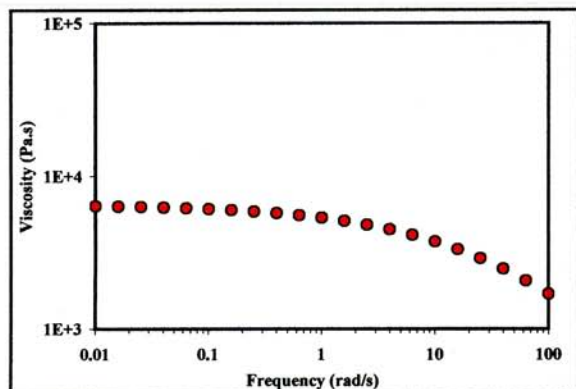
(a)



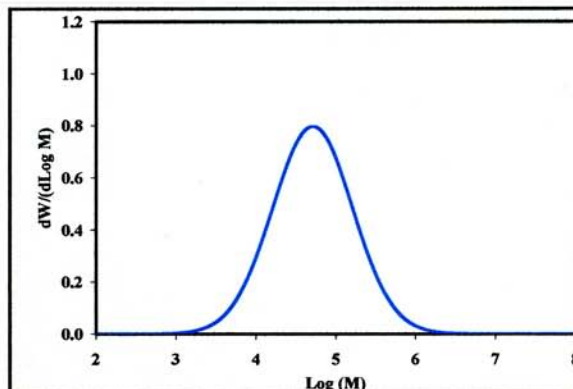
(b)

**Figure 1. (a) Complex viscosity versus frequency at 190 °C and (b) GPC traces, for resins L1, L2, L3 and L4.**

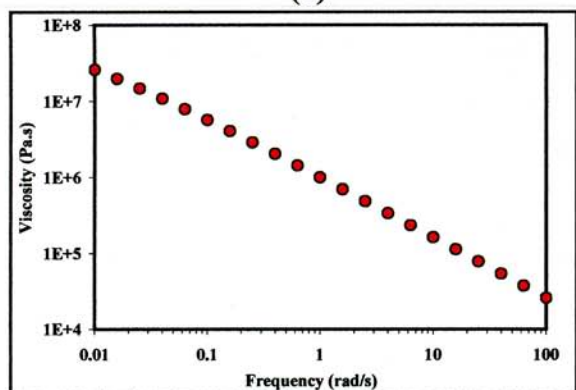




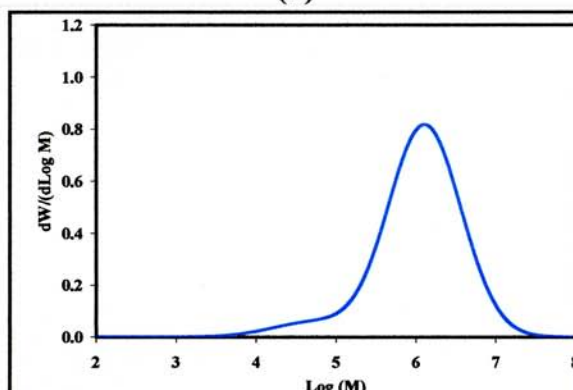
(a)



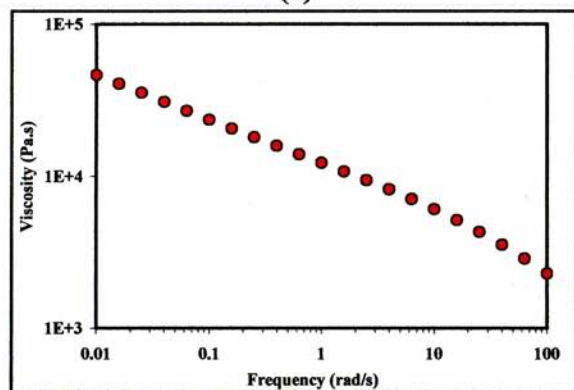
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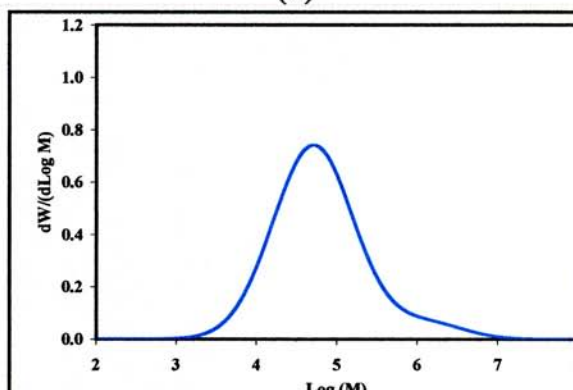
(c)



(d)



(e)



(f)

**Figure 2.** Rheology and GPC simulated curves for three cases: (1) – single component with a log-normal Gaussian GPC distribution, (a) and (b), (2) two component blend with the higher  $M_w$  component being 93 wt % of the total, (c) and (d) and (3) same two components as in case 2, but with the higher  $M_w$  component now being 7 wt % of the total, (e) and (f). Case 3 generates a “S-shaped” viscosity curve, with a tendency for the low shear viscosity to increase somewhat abruptly which is not observed in case 2. Note also the similarities between the rheology and GPC traces for simulation 3 compared to experimental resin L3 in Figure 1.

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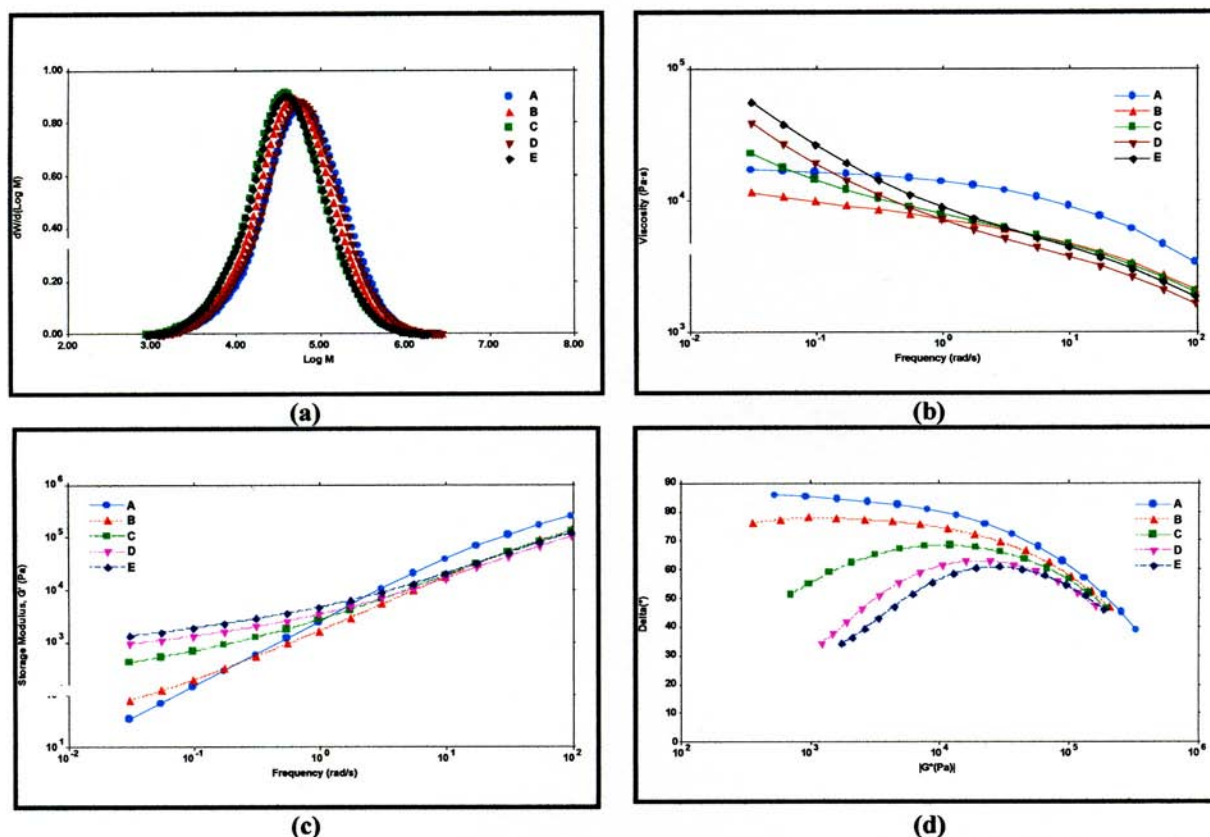


Figure 3. Various data for experimental resins A through E: (a) GPC traces of resins, (b) complex viscosity versus frequency, (c) storage modulus versus frequency and (d) loss angle ( $\delta$ ) versus complex modulus data. Note the very sharp upturn in the complex viscosity at lower frequencies for samples C, D and E (Fig. 4b), the leveling off in the storage modulus at lower frequencies for samples C, D and E (Fig. 4c) and the clear maxima in the loss angle versus complex modulus curves for samples C, D and E (Fig. 4d).

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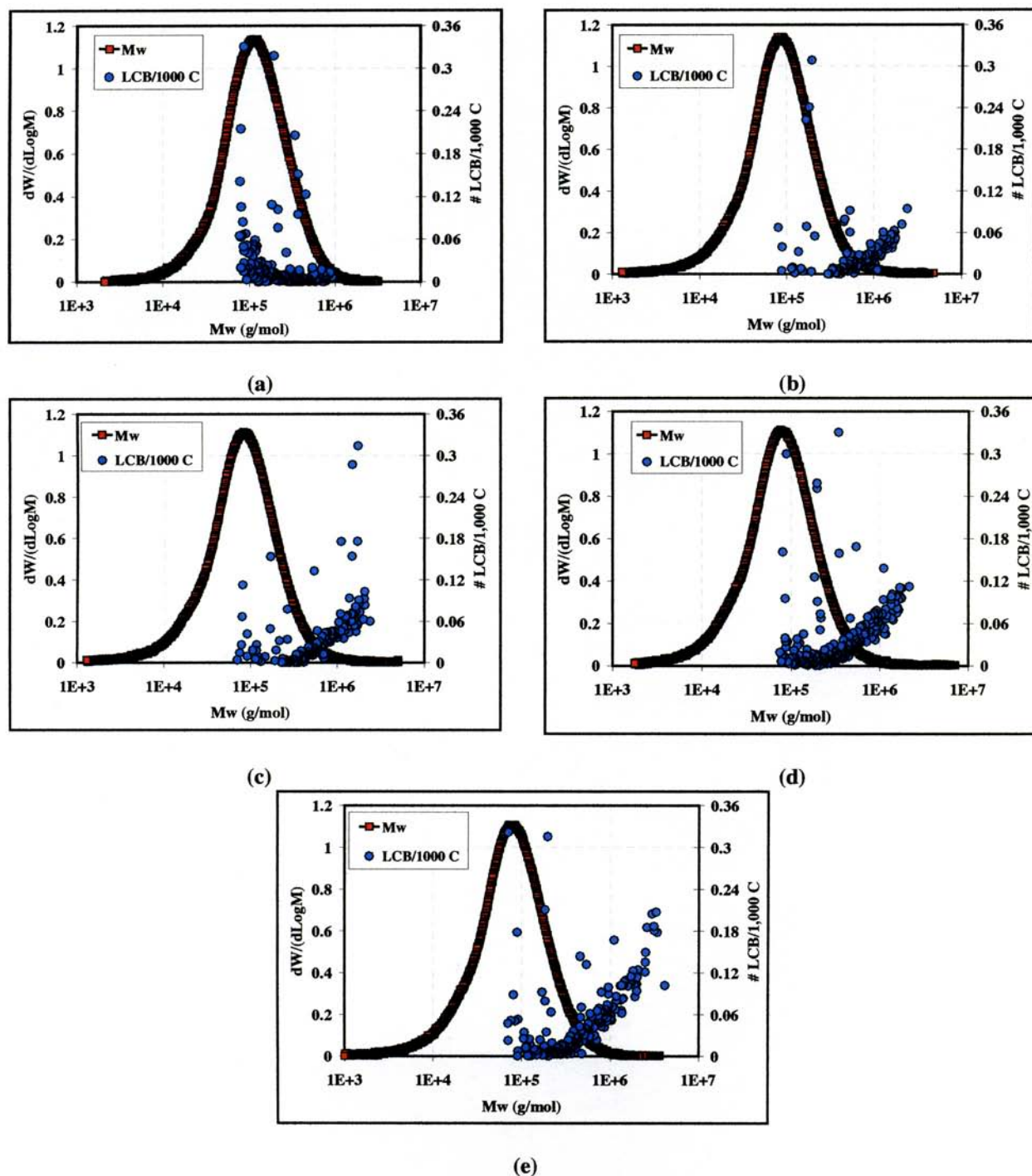


Figure 4. GPC and long chain branching (LCB) content from SEC-MALS characterization for samples (a) A, (b) C, (d) D and (e) E. Note the systematic increase in the LCB content going from samples A to E.



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