

GPC Determination of Molecular Weights for EPM, EPDM, and Polybutadienes

WENDELL V. SMITH, *Uniroyal, Inc., Oxford Management and Research Center, Middlebury, Connecticut 06749*

Synopsis

Molecular weights from GPC curves are determined for EPM, EPDM, and some polybutadienes. The determinations make use of a Benoit factor, B , which is defined and tabulated for the polymers studied. The use of this factor provides a convenient method of employing the Benoit hypothesis. The \bar{M}_n from the GPC curves are compared with osmotic molecular weights to provide additional confirmation of the Benoit hypothesis. The \bar{M}_w from the GPC curves are used with intrinsic viscosity data to establish $[\eta]$ -versus- M relations.

INTRODUCTION

During the past few years, GPC has become the most convenient and most informative method of determining the molecular weight of polymers.¹ This report describes the use of GPC in determining the molecular weights of some EPM, EPDM, and butadiene polymers.

In converting the GPC data to molecular weights, use is made of the Benoit hypothesis.² This is done through use of quantities which we are proposing to call the "Benoit factors." The values of these factors for the polymers studied are given. The GPC molecular weights obtained are compared with osmotic pressure molecular weights to obtain additional confirmation of the applicability of the Benoit hypothesis. They are also used to determine the intrinsic viscosity-molecular weight relationships.

The $[\eta]$ -versus- M relation for EPM has recently been reviewed by Baldwin and Ver Strate.³ We believe that the relations established in the present investigation are improvements over the previously published relations. Data on polybutadienes have been reviewed by Kurata, Iwama, and Kamada.⁴ Our data on the high-cis polybutadienes are in substantial agreement. Our data on the butyllithium polybutadienes confirm clearly the effect of well-characterized branching on intrinsic viscosity.

EXPERIMENTAL

Polymers

The most important descriptive information on the ethylene-propylene copolymers and terpolymers is given in Table I. All of the individual sam-

TABLE I
Ethylene Propylene Polymers

Sample no.	Polymer designation	Termonomer	Propylene, %
1 to 17	A	none	52
18 to 27	B	ethylidenenorbornene	48
28 to 32	C	ethylidenenorbornene	39
33	D	ethylnorbornene	47
34	E	dicyclopentadiene	35

TABLE II
Butadiene Polymers

Sample no.	Type	<i>cis</i> , %	<i>trans</i> , %	Vinyl %
35 to 43	butyllithium	40	50	10
44 to 45	butyllithium (branched)	40	50	10
46 to 48	phenylmagnesium	97	0	3
49 to 52	Taktene	>90		

ples except samples 12 and 13 are fractions obtained by column elution fractionation. Typical conditions for carrying out such a fractionation are discussed by Smith and Thiruvengada.⁵ When fractionation did result in some change in propylene content of some of the samples, it was not large and we are not detailing the data. Samples 12 and 13 were preparative GPC fractions; they were not as narrow in distribution as the others.

The butadiene polymers are described in Table II. The butyllithium polymers, samples 35 to 43, were used as made without fractionation. This type of polymerization results in extremely narrow molecular weight distribution. Samples 44 and 45 were branched butyllithium polymers. They were prepared by first forming butyllithium polymer "arms" with reactive endgroups. Four endgroups were then united with a tetrafunctional coupling agent. Since their coupling was not complete, a column elution fractionation was carried out and the highest molecular weight portion retained. Narrow fractions of four-arm star-branched polymer resulted. The four arms should all be of the same length since there was little spread in distribution in the uncoupled starting polymer.

The phenylmagnesium polymers, samples 46 to 48, were fractions by column elution fractionation. The Taktene fractions, samples 49 to 52, were those described previously.⁵

The polystyrenes used were Pressure Chemical standard polystyrenes used without fractionation.

Osmotic Pressure

The osmotic pressures were run in a Hewlett-Packard Model 501 high-speed membrane osmometer. Extrapolations of π/c to zero concentration were linear using measurements at four concentrations. The membranes

used were cellulose acetate. Results for samples having molecular weights greater than about 3×10^5 appeared to be unreliable and are not included in the tables.

Intrinsic Viscosity

Intrinsic viscosities were run in several solvents and at different temperatures. Ubbelohde viscometers with flow times greater than 100 sec were used. For most of the data, the necessary extrapolations to zero concentration were made from measurements at four concentrations. In some cases, only one concentration was measured and an assumed extrapolation employed. The results gave no indication of a desirability of distinguishing between four-point and one-point intrinsic viscosities.

GPC Measurements

GPC measurements were carried out in Water's Associates Model 200 instruments using 0.05% solutions of polymer. During the course of this work, three different instruments were used. Most of the measurements were made with the usual four-column assembly (10^6 , 10^5 , 10^4 , 10^3) using flow rates of 1 ml/min or 2 ml/min. However, some of the measurements were done with either two columns or a special single column of mixed Styragel with a flow rate of 6 ml/min. At various times, two different solvents were used: tetrahydrofuran (THF) at 30°C and orthodichlorobenzene (*o*-DCB) at 130°C. Calibrations with polystyrene standards were carried out using all of the combinations of conditions used in running the various samples.

Two of the samples, 5 and 11, were run under several of the conditions described above, with results given in Table III. In the case of the single column, a fast flow rate, 6 ml/min, was used. The value of M_s given in the table is the molecular weight read off the appropriate calibration curve prepared from standard polystyrenes. With the possible exception of a solvent effect, the conditions do not appear to have an appreciable effect on the molecular weight obtained. In principle, the value of M_s can be a function of the solvent; but the data in the table show that it is not a strong function when comparing THF with *o*-DCB.

TABLE III
Comparison of GPC Molecular Weights Obtained Under Different Conditions

Columns	$M_s \times 10^{-5}$				
	THF at 30°C			<i>o</i> -DCM at 130°C	
	1	4		4	
Instrument	#3	#1	#2	#1	#2
Sample 5	1.15	1.05	1.00	1.10	1.04
Sample 11	3.1	3.0	3.30	3.70	3.75

Data

The principle experimental data are given in Tables IV and V. The value of peak M_s obtained from the GPC curve is that obtained by converting to molecular weight the elution volume corresponding to the peak of the GPC curve. The conversion of elution volume to molecular weight is done using the appropriate calibration curve of M versus V obtained using polystyrene standards. Thus, it is the molecular weight of polystyrene which has an elution volume the same as that corresponding to the peak of the GPC curve. We call this a polystyrene equivalent peak molecular weight, peak M_s . The average molecular weights used in calculating the ratios for the last two columns of Table IV were obtained from the GPC curves using the following summations:

$$[(\bar{M}_s)_n]_u = \Sigma H / \Sigma (H/M_s) \quad (1)$$

and

$$[(\bar{M}_s)_v]_u = (\Sigma H M_s^{0.7} / \Sigma H)^{1/0.7} \quad (2)$$

where H is the height of the GPC curve at the elution volume corresponding to the polystyrene equivalent molecular weight M_s . The subscript u on the averages indicates that no correction for instrumental spreading has been made. The problem of correcting these molecular weight averages for instrumental spreading has been discussed,⁶ and this correction has been applied to obtain the values given in the last two columns of Table IV. In making this correction for the four GPC columns, the value for the molecular weight correction factor, $\bar{G}(1)$, was taken to be 1.08, i.e., the value given in our previous publication.⁶ Thus,

$$(\bar{M}_s)_n = 1.08 [(\bar{M}_s)_n]_u \quad (3)$$

and

$$(\bar{M}_s)_v = [(\bar{M}_s)_v]_u / 1.08^{1/0.7} \quad (4)$$

For the one and two GPC columns, $\bar{G}(1)$ was taken to be 1.17.

Since they have been corrected for instrumental spreading, the ratios in the last two columns of Table IV are good measures of the breadth of the molecular weight distributions. It is seen that in most cases the molecular weight distributions of these fractions are reasonably narrow. In particular, in most cases the viscosity-average molecular weight does not depart much from the molecular weight corresponding to the peak of the GPC curve.

In the case of the polybutadiene samples of Table V, the butyllithium polymers were very narrow in molecular weight distribution as they were prepared. Thus, the GPC widths at half-height were all substantially less than that for the EPM sample 6 of Table IV. Since most of the original GPC curves were no longer available when we analyzed the data, we do not give values for $(\bar{M}_s)_n/M_s$ and $(\bar{M}_s)_v/M_s$ but have taken these to be unity in the subsequent use of the data. This introduces some uncertainty, but it is not a serious source of error. In the case of the typical Taktene frac-

tion, sample 50, we have the necessary data to obtain $(\bar{M}_s)_n/M_s = 0.90$ and $(\bar{M}_s)_v/M_s = 1.01$.

Some additional intrinsic viscosity data were obtained on the EPR samples 5 and 11. These data are given in Table VI. Also, the intrinsic vis-

TABLE IV
Experimental Data on EPM and EPDM

Sample no.	[η]		\bar{M}_n osmotic $\times 10^{-5}$	GPC		
	Toluene 30°C	Tetralin 135°C		Peak M_s $\times 10^{-5}$	$(\bar{M}_s)_v/M_s$	$(M_s)_n/M_s$
<i>EPM, Sample A</i>						
1	0.52	0.53		0.55	1.19	0.80
2			0.355	0.67	1.03	1.04
3	0.65			0.74	1.09	0.97
4	0.76	0.81		0.84	1.29	0.90
5	0.863	0.887	0.51	1.085	1.13	0.84
6		0.89	0.74	1.31	0.97	0.95
7	0.95	1.02				
8	1.00	1.06		1.33	1.13	0.85
9		1.35	1.64	2.58	0.93	0.86
10	1.59	1.69				
11	1.770	1.960	1.99	3.39	1.03	0.77
12	1.87			3.0	1.31	0.69
13	2.08	2.25		4.0	1.25	0.62
14		2.30	2.65	4.30	0.93	0.83
15			2.33	4.35		0.87
16	2.42	2.56		4.63	1.01	0.77
17	3.25	3.37		6.25	1.20	0.80
<i>EPDM, Sample B, 48% P</i>						
THF 30°C						
18	0.48		0.21	0.50	1.02	0.92
19	.68			.95	(1.0)	
20	.91	.91	.74	1.4	.99	.93
21	1.17			2.1	1.00	.81
22	1.78	1.70	2.35	3.5	.97	.89
23	1.97		2.45	4.5	.95	.77
24	2.73	2.70		6.9	.97	.86
25	2.75			7.9	.99	.94
26		3.10		9.7	1.02	.83
27	3.88			14	1.06	.82
<i>Sample C, 39% P</i>						
28	0.65		0.25	0.56	1.00	0.94
29	0.84		0.56	0.96	0.96	0.88
30	1.38		1.23	1.85	1.02	0.93
31	2.17			4.05	1.05	0.84
32	3.33			7.8	1.19	0.95
<i>Ethylnorbornene Terpolymer</i>						
33			2.29	4.4		0.86
<i>Dicyclopentadiene Terpolymer, Sample E</i>						
34			2.51	4.6		0.83

TABLE V
Experimental Data on Polybutadienes

Sample no.	[η]		\bar{M}_n Osmotic $\times 10^{-5}$	GPC peak M_n $\times 10^{-5}$
	Toluene 30°C	THF 30°C		
<i>Butyllithium Polybutadiene</i>				
35	0.52	0.56	0.26	0.54
36	0.97	1.01	0.67	1.22
37	1.40	1.39	1.22	1.85
38	1.38	1.59	1.06	2.20
39	2.10	2.14	2.00	3.30
40	2.52	2.52	1.82	4.5
41	2.68	2.91	2.69	5.0
42	3.92	4.11		8.0
43	6.08	6.68		15.5
<i>Bu-Li Four-Arm Star-Branched Polybutadiene</i>				
44	1.30	1.36		2.25
45		3.24		8.00
<i>Phenylmagnesium, High-Cis</i>				
46	1.95			4.0
47	3.32			6.8
48	4.22			10.5
<i>Taktene</i>				
49			0.27	0.45
50	1.00		0.97	1.50
51	1.86		2.65	3.65
52	3.59			9.65

TABLE VI
Intrinsic Viscosities of EPM in Other Solvents

Sample no.	Intrinsic viscosity	
	THF at 30°C	<i>o</i> -DCB at 135°C
5	0.896	0.830
11	1.856	1.752

cosities of standard polystyrenes were obtained in THF at 30°C and *o*-DCB at 135°C. The results of these are presented in the next section.

Interrelations

In making use of the Benoit hypothesis to get molecular weights from GPC data, it is convenient to have the relation between molecular weight and intrinsic viscosity for polystyrene in the GPC solvents used. Our data on this relation obtained using the polystyrene standard calibration samples yield the equations.

$$[\eta] = 1.112 \times 10^{-4} M^{0.723} = 0.458 (M/10^5)^{0.723}$$

(polystyrene in THF at 30°C) (5)

TABLE VII
 Constants Relating Intrinsic Viscosities in Different Solvents^a

Polymer	Solvents		α	β	Standard error, %
	A	B			
Polystyrene	<i>o</i> -DCB at 135°C	THF at 30°C	0.94	0.99	3.9
EPDM	THF	toluene	1.016	0.972	4.2
or EPM	tetraline at 135°C	toluene	1.055	1.014	2.5
	<i>o</i> -DCB at 135°C	toluene	0.98	1.0	(2 points)
Polybutadiene	THF	toluene	1.055	1.001	5.3

^a See eq. (7).

with a standard error of 4.6%, and

$$[\eta] = 1.156 \times 10^{-4} M^{0.715} = 0.434 (M/10^5)^{0.715}$$

(polystyrene in DCB at 135°C) (6)

with a standard error of 3.3%. The values of the constants were obtained from a least-squares fit of a linear ln–ln relation.

It is also frequently convenient to be able to estimate the intrinsic viscosity in one solvent from a value measured in another solvent. This can be done making use of experimentally determined constants in the relation

$$[\eta]_A = \alpha([\eta]_B)^\beta \quad (7)$$

where *A* and *B* refer to the two different solvents and α and β are experimental constants. Table VII contains values of the constants obtained from the intrinsic viscosities given in Tables IV, V, and VI.

GPC MOLECULAR WEIGHT

Method of Calculation

The GPC curve represents the incremental fraction of polymer being eluted as a function of the elution volume *V*. It is related to the molecular weight distribution curve because the elution volume is related to molecular weight. Benoit and co-workers² have proposed and offered supporting evidence that the polymer property important in determining *V* is the hydrodynamic volume of the polymer in the GPC solvent. Since this hydrodynamic volume in turn is primarily a function of the product of the intrinsic viscosity and the molecular weight, i.e., $[\eta]M$, the Benoit hypothesis can be stated as

$$V = f([\eta]M) \quad (8)$$

where *V* is the elution volume and *f* is some function which involves polymer properties only through $[\eta]$ and *M*.

Of course, $[\eta]$ refers to intrinsic viscosity in the GPC solvent. Thus, if we have two polymers which exhibit the same elution volume, then

$$[\eta]_1 M_1 = [\eta]_2 M_2.$$

TABLE VIII
Benoit Factors and GPC Molecular Weights (Ethylene Propylene Polymers)

Sample no.	Benoit factor B	$\bar{M}_v \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$
<i>EPM, Sample A</i>			
1	0.62	0.373	
2			0.44
3	0.59	0.50	
4	0.62	0.68	
5	0.60	0.77	0.57
6			0.78
8	0.60	0.94	
9			1.39
11	0.64	2.18	1.63
12	0.66	2.45	
13	0.71	3.12	
14			2.24
15			2.36
16	0.58	2.92	
17	0.62	4.67	
	av. 0.624		
<i>EPDM, Sample B, 48% P</i>			
18	0.56	0.290	0.274
19	0.63	0.60	
20	0.64	0.88	0.83
21	0.66	1.38	
22	0.65	2.16	1.97
23	0.66	2.66	2.16
24	0.67	4.32	
25	0.75	5.85	
26	0.77	7.7	
27	0.85	13.4	
<i>EPDM, Sample C, 39% P</i>			
28	0.45	0.252	0.237
29	0.50	0.44	0.423
30	0.52	1.00	0.92
31	0.60	2.68	
32	0.70	7.7	

If the second polymer is polystyrene, we can denote its molecular weight by M_s , and its intrinsic viscosity by $[\eta](s)$ so that

$$M = M_s[\eta](s)/[\eta]. \quad (9)$$

M_s is the molecular weight which is directly determinable from the elution volume by means of the calibration curve of M_s versus V obtained for polystyrene standards. To convert this to the molecular weight of the polymer of interest, it is necessary to know the value of the ratio $[\eta](s)/[\eta]$. The importance of this ratio in making use of the Benoit hypothesis is now evi-

TABLE IX
Benoit Factors and GPC Molecular Weight (Polybutadienes)

Sample no.	Benoit Factor B	GPC mol. wt. $\times 10^{-5}$
<i>Polybutadiene-Butyllithium</i>		
35	0.53	0.28
36	0.52	0.63
37	0.51	0.96
38	0.51	1.14
39	0.55	1.71
40	0.54	2.34
41	0.51	2.60
42	0.50	4.15
43	0.50	8.05
	ave. 0.519	
<i>Four-Arm Star-Branched</i>		
44	0.61	1.39
45	0.63	4.96
	ave. 0.62	
<i>Phenylmagnesium, High-cis</i>		
46	0.61	2.27
47	0.52	3.86
48	0.57	5.95
	ave. 0.57	
<i>Taktene</i>		
49		0.28
50	0.65	.94
51	0.60	2.27
52	0.62	6.01
	ave. 0.62	

dent. It is convenient to adopt a less cumbersome symbol for this, and we are suggesting that it be called the Benoit factor with a symbol B, so that

$$B = [\eta](s)/[\eta] \quad (10)$$

where $[\eta](s)$ is the intrinsic viscosity of polystyrene having the same elution volume as that of a polymer of interest which has an intrinsic viscosity of $[\eta]$. It is understood that both intrinsic viscosities refer to the GPC solvent.

Numerical values for these Benoit factors for the polymers studied are given in Tables VIII and IX. In calculating these, first the value of $[\eta](s)$ was obtained for the polystyrene equivalent viscosity-average molecular weight of the sample. This molecular weight was obtained from

$$(\bar{M}_s)_v = M_s \times (\bar{M}_s)_v / M_s \quad (11)$$

where M_s refers to the value at the peak of the GPC curve; both M_s and $(\bar{M}_s)_v/M_s$ are tabulated in Table IV. In treating the data of Table V, it was assumed that $(\bar{M}_s)_v = \text{peak } M_s$. Then, from $(\bar{M}_s)_v$ the value of $[\eta](s)$ was obtained from eq. (5) or (6) depending on which solvent was used in the GPC. The value of $[\eta]$ for the sample in the GPC solvent was that given in the experimental data of Tables IV and V; or, if only data in another solvent were available, the necessary conversions were made using eq. (7) and the constants given in Table VII. In the case of some of the polymer types, B appears to be independent of molecular weight, so an average value is given in the tables. However, in the case of the EPDM polymers, there appears to be an upward trend in B with increase in molecular weight, so an average is not useful.

The GPC molecular weight averages given in the tables were obtained from

$$\bar{M}_v = BM_s \times (\bar{M}_s)_v/M_s \quad (12)$$

and similarly for \bar{M}_n . The values of M_s and $(\bar{M}_s)_v/M_s$ are obtained from Tables IV and V, and B is either an average B or an individual sample B as given in Tables VIII and IX. Average B's were used except for the EPDM samples B and C, where it was felt that the obvious drift in B values did not justify using an average. Not all the possible molecular weight averages are given, only those which are used later to compare with osmotic molecular weight or with intrinsic viscosities.

Test of Benoit Hypothesis

Many data have already been published which support the Benoit hypothesis. Since the GPC \bar{M}_n values of Tables VIII and IX were calculated using this hypothesis, they can be compared with the osmotic molecular weights of Tables IV and V to offer additional confirmation of the applicability of the hypothesis to ethylene propylene polymers and polybutadienes. We have analyzed all the pertinent data together since there did not appear to be any difference between the data for the different polymers. In order to make use of the osmotic pressure data for samples 33 and 34, it was necessary to estimate B values to get $\bar{M}_n(\text{GPC})$. Since the necessary intrinsic viscosity information was not available, the value of $\bar{M}_n(\text{GPC})$ estimated for both samples was 2.4×10^{-5} . All the data were analyzed to minimize the squares of the deviations of the logarithms, thus obtaining

$$\bar{M}_n \times 10^{-5} (\text{osmotic}) = 0.969[\bar{M}_n \times 10^{-5}(\text{GPC})]^{0.918} \quad (13)$$

with a standard error of 15.4%. The greatest deviation of this equation from the anticipated Benoit relation (osmotic $\bar{M}_n = \text{GPC } \bar{M}_n$) is 12% in the range covered by the experimental data. Thus, the data offer good support to the validity of the Benoit hypothesis.

Intrinsic Viscosity-Molecular Weight Relation

The relation between intrinsic viscosity $[\eta]$ and molecular weight M can be expressed in the forms

$$[\eta] = KM^\alpha = K'(M \times 10^{-5})^\alpha \quad (14)$$

TABLE X
Intrinsic Viscosity-Molecular Weight Relations (see Eq. (14))

Polymer	Solvent	K'	$K \times 10^4$	α	Standard error, %
Polystyrene	THF	0.458	1.112	0.723	4.6
	<i>o</i> -DCB at 135°C	.434	1.156	0.715	3.3
EPM	toluene	1.034	3.051	0.706	5.6
Sample C, 39% P	toluene	1.4	curvature in region 10^5 - 10^6		
Sample B, 48% P	toluene	1.0			
Polybutadiene (butyllithium)	toluene	1.351	2.888	0.734	4.6
Star-branched	toluene	1.02	(2 points)		
Taktene	toluene	1.05	(3 points)		
High- <i>cis</i> (phenyl Mg)	toluene	~ 1.2	(3 points)		

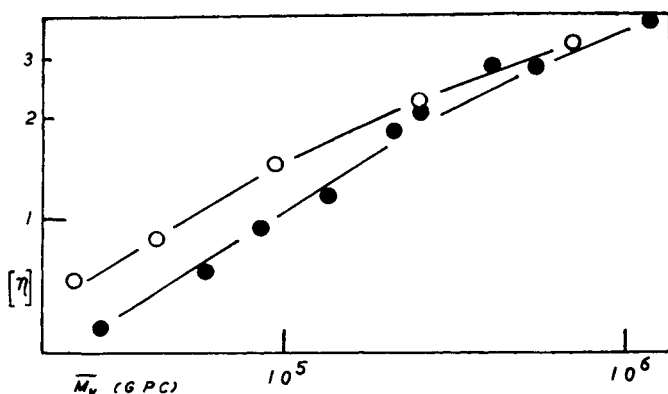


Fig. 1. Intrinsic viscosity-molecular weight relationship for: (O) sample C (39% propylene); (●) sample B (48% propylene).

The first part is the usual expression, but the second is frequently more convenient for comparing polymers. In the second form, K' is simply the intrinsic viscosity at molecular weight 10^5 . For elastomers, this is a convenient molecular weight for comparison. For significant values of the constants, the molecular weight in eq. (14) should be for a monodisperse sample. Real samples have a molecular weight distribution, in which case a viscosity-average molecular weight \bar{M}_v should be used to evaluate the constants.

The intrinsic viscosities of Tables IV and V have been combined with the GPC molecular weights of Tables VIII and IX to evaluate the constants of eq. (14). Again in analyzing the data, the constants were chosen to minimize the squares of the deviation of the logarithms. The values found for the constants are given in Table X. In four cases, no value is given for the exponent α because of limited data or because of an indicated curvature. In these cases, for the value of K' , the estimated intrinsic viscosity at $M = 10^5$ is given. To demonstrate the indicated curvature, the data for the

EPDM samples B and C are plotted in Figure 1. None of the other polymers gave indications of curvature.

DISCUSSION

We have illustrated the use of the Benoit factor in obtaining molecular weights from GPC data. A systematic determination of them for a variety of polymers should be very useful. The data given in Tables VIII and IX might suggest that for normal polymers the Benoit factor may be practically independent of molecular weight. The apparent variation in the case of the EPDM samples could be a result of the fractionation. Thus fractionation may not be solely by molecular weight, but structural factors may also vary in the fractions. The curvature in the $[\eta]-M$ relation (Fig. 1) may also result from this.

From its concept, the Benoit factor should be affected by the same structural factors that influence the intrinsic viscosity. Thus, more compact molecules should have larger Benoit factors.

To compare the present $[\eta]-M$ relation with previous data, it is convenient to calculate the constants for tetralin at 135°C. This can be done using data of Table VII to obtain the constants for eq. (14). Thus, for EPM (50% propylene) in tetralin at 135°C, the present data give $K' = 1.09$ and $\alpha = 0.72$. These may be compared with the comparable values quoted by Baldwin and Ver Strate.³ Converting their K to K' ($[\eta]$ at $M = 10^5$), the values obtained from the work of Imoto and co-workers are $K' = 1.56$ and $\alpha = 0.73$, while from the work of Moraglio, $K' = 1.58$ and $\alpha = 0.74$. The value from Keim's data is even higher, $K' = 1.80$, when converted from decalin to tetralin. Thus, we find considerably lower intrinsic viscosities in the region of $M = 10^5$ than the others cited. However, the relation which Baldwin and Ver Strate quoted based on our previous light-scattering work gives $K' = 1.06$, which is in good agreement with the present data based on GPC molecular weights.

When the EPM copolymer is compared with the ethylidinenorbornene terpolymer having about the same propylene content (48%), it is seen that the intrinsic viscosities at $M = 10^5$ are very similar, i.e., $K' = 1.03$ versus 1.0 (Table X). Thus, the introduction of the termonomer has little effect on the intrinsic viscosity below $M = 10^5$, but it may be responsible for curvature in the $[\eta]-M$ relation above $M = 10^5$. As has already been mentioned this could result from branching. The difference is not well established, however, because the EPM data did not extend to as high a molecular weight.

There is quite clearly an effect of propylene content on intrinsic viscosity as would reasonably be expected. Thus, for the EPDM polymers, the value of K' for the 48% propylene group is 1.0 compared with 1.4 for the 39% propylene group (Table X).

During the course of this investigation, some additional scattered data were obtained which are not given in detail here. Some ethylnorbornene

terpolymers had about the same Benoit factors and $[\eta]$ - M relation as the EPM samples. Hydrogenation of the double bond in an ethylidene-norbornene terpolymer did not noticeably affect the intrinsic viscosity.

The K' value for the butyllithium polybutadiene given in Table X, 1.35, lies above the value of 1.29 obtained from the data for a high-cis polybutadiene given in Bandrup and Immergut.⁴ It is expected that it should be higher because of its greater trans content. Our data for the high-cis phenylmagnesium polymer gives a K' value of about 1.2, which is in satisfactory agreement with the previous value.

It is known that branching leads to a decrease in intrinsic viscosity, and this is clearly shown by K' values in Table X. K' for the four-arm star-branched polybutadiene is 1.02, compared with 1.35 for the comparable unbranched butyllithium polymer.

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