

# Mark-Houwink Equation and GPC Calibration for Linear Short-Chain Branched Polyolefins, Including Polypropylene and Ethylene-Propylene Copolymers

TH. G. SCHOLTE, N. L. J. MEIJERINK, H. M. SCHOFFELEERS, and  
A. M. G. BRANDS, *Central Laboratory, DSM, Geleen,  
The Netherlands*

## Synopsis

The reduction in molecular dimensions due to the presence of short side chains in otherwise linear polyolefins can very simply be calculated by assuming that the configuration of the main chain is not influenced by the side chains. This enables us to express the intrinsic viscosity-molar mass relationship as a function of the mass fraction of side chains ( $S$ ):  $[\eta] = (1 - S)^{\alpha+1} K_{PE} M_w^{\beta}$  and, with use of the universal calibration principle, to convert the GPC calibration for purely linear polymer samples into the calibration for short-chain branched polymers:  $M^* = (1 - S)M$ . Experimental data from literature on short-chain branched polyethylenes, and our own data on ethylene-propylene copolymers are used to verify the above assumption. It appears that the experimentally found relations between  $[\eta]$ ,  $M_w$  and  $M^*_w$  (GPC) within the usual accuracy justify this approach.

## INTRODUCTION

While gel permeation chromatography (GPC) of a polymer sample gives its distribution over elution volumes (the chromatogram), conversion to the molar mass distribution requires calibration for the type of polymer under investigation. This presupposes the availability either of a series of suitable polymer standards, or of calibration data for another type of polymer, in which latter case the calibration for the polymer under study is calculated on the universal calibration principle, making use of the constants of the Mark-Houwink equations for both polymers in the GPC solvent. This procedure is especially convenient if closely related polyolefins, such as polyethylene, polypropylene, and ethylene-propylene copolymers are successively studied in one GP chromatograph. "Built-in" absolute calibration by on-line detection of  $M_w$  by additional light scattering would be very convenient too, but for routine measurements this is as yet difficult to realize.<sup>1,2</sup>

With polymers showing long-chain branching (LCB) the combination of absolute molar mass  $M_w$  (mostly obtained from light scattering) and intrinsic viscosity data provides the possibility to determine an LCB index ( $g' = [\eta]/[\eta]_{lin}$ ), on condition that the constants of the Mark-Houwink equation for the linear polymer are accurately known. However, such an LCB index can also be derived from a combination of GPC data, and either the intrinsic viscosity or the  $M_w$  of the sample (although, especially with samples having

a broad distribution, this leads to different averages for the  $g'$  of the sample<sup>3,4</sup>). GPC combined with on-line viscometry or on-line light scattering measurements enables the LCB index  $g'$  to be determined as a function of the molar mass. Although there are still many difficulties on this point—mainly in respect of theory—it is possible to calculate the ratio between the mean square radii of gyration of a linear and a branched molecule with the same molar mass ( $g$ ) from the LCB index  $g'$ , and, by means of the formulas of Zimm and Stockmayer<sup>5</sup> for various dispersities, types of LCB and branching functionalities, to derive from this ratio the number of long side chains per unit of molar mass, that is, the branching frequency  $\lambda$ . In these derivations the index  $g'$  must be corrected for the influence of short-chain branching (SCB).<sup>6,7</sup>

For otherwise-linear polymers with short-chain branching only, Stockmayer a long time ago already derived a formula<sup>8</sup> presenting the decrease of the radius of gyration at constant molar mass as a function of the number and length of the short side chains. Also several other authors<sup>7,9-13</sup> have studied the influence of SCB on the molar dimensions, hence on  $g$  and  $g'$ . In a very simple hypothesis short side chains (chains with fewer than six C atoms) do not influence the mobility of the backbone, nor do they make any other contribution to the molecular dimensions within the accuracy of measurement. The influence of SCB on Mark-Houwink constants and GPC calibration can then very easily be derived from the weight fraction of the short side chains. Below we will investigate if, and to what degree, experiments bear out this working hypothesis. It will also be investigated what conversion factors should be used for elaborating the GPC results for short-chain branched polyethylenes (including LLDPE samples) as well as for ethylene-propylene copolymers and what correction factors should be applied for determining the degree of long-chain branching.

### RELATION BETWEEN MOLAR MASS, MOLECULAR DIMENSIONS, AND INTRINSIC VISCOSITY

The relative increase in the viscosity of a solvent brought about by addition of polymer molecules is reflected in the intrinsic viscosity. The latter is related to molar mass and molecular dimensions by the formula of Flory and Fox<sup>14</sup>:

$$[\eta]M = 6^{3/2}\Phi\langle R^2 \rangle^{3/2} \quad (1)$$

For the unperturbed state this leads to

$$[\eta] = K \cdot M^{1/2} \quad (2)$$

For solutions of a polymer in a good solvent the influence of the coil expansion is taken into account in the equation of Stockmayer and Fixman<sup>15-17</sup> and in the more commonly used Mark-Houwink (Kuhn-Mark-Houwink-Sakurada) equation<sup>18</sup>:

$$[\eta] = KM^a \quad (3)$$

Because the molecular dimensions are given by the product  $[\eta]M$ , and GPC (SEC) generally effects a separation according to molecular dimensions, the

elution volume of a GPC fraction (for a given solvent and given temperature) bears a unique relation to the product  $[\eta]M$  (principle of universal calibration<sup>19</sup>). If, for instance, use is made of calibration with linear polyethylene, calculation of  $M$  from the elution volume will give the molar mass of linear polyethylene, leaving the columns at this particular elution volume (defined as  $M^*$ ; the intrinsic viscosity of this linear polyethylene is  $[\eta]^*$ ). If the constants ( $K$  and  $a$ ) of the Mark-Houwink equation for the polymer concerned and for the linear polyethylene are known,  $M^*$  can be reduced to  $M$  by use of

$$[\eta]M = [\eta]^*M^* \quad (4)$$

which leads to

$$M = \left[ (K_{PE}/K(M^*)^{a_{PE}+1}) \right]^{1/(a+1)} \quad (5)$$

In the case of polydisperse polymers the Mark-Houwink equation is valid for each of the components. If the sample consists of components  $i$  with mass fraction  $f_i$ , then

$$[\eta] = \sum_i f_i[\eta]_i = \sum_i f_i KM_i^a = KM_v^a \quad (6)$$

However, the mean molar mass mostly determined in experiments is not  $M_v$  but  $M_w$ . The  $M_v/M_w$  ratio can be calculated exactly from the molar mass distribution and is, roughly, a function of the width of this distribution ( $M_w/M_n$ ). For a log-normal distribution it has been calculated<sup>20</sup> that

$$\frac{M_v}{M_w} = \left( \frac{M_w}{M_n} \right)^{-(1-a)/2} \quad (7)$$

Equation (6) may also be written as

$$[\eta] = KM_w^a \left( \frac{M_w}{M_n} \right)^{-p} \quad (8)$$

where, with a log-normal distribution for  $a = 0.725$ , the exponent  $-p$  equals  $-a(1-a)/2 \approx 0.10$ . As with other types of distribution  $p$  is generally slightly lower, a somewhat different exponent, e.g.,  $-p = -0.07$ , may be used in practice.

### INFLUENCE OF SHORT SIDE CHAINS ON MOLECULAR DIMENSIONS

If it is assumed that, in linear macromolecules having short side chains only, these side chains do not affect the conformation of the backbone nor do they make any contribution to the molecular dimensions within the

accuracy of measurement, it must be concluded that the molar dimensions are equal to those of the backbone alone. If the mass fraction of the short side chains is  $S$ , then a polyolefin molecule showing exclusively SCB and having a mass  $M$  has the same dimensions as a purely linear polyethylene molecule with mass  $M(1-S)$ . A direct consequence is then<sup>21</sup>

$$M^* = M(1-S) \quad (9)$$

From the equation for universal calibration,

$$[\eta]M = [\eta]^*M^* \quad (4)$$

and (assuming the same exponent to hold for both polyolefins) the Mark-Houwink equations for the SCB polyolefin,

$$[\eta] = KM^a$$

and linear polyethylene,

$$[\eta]^* = K_{PE}(M^*)^a$$

it then follows that

$$\frac{K}{K_{PE}} = \left(\frac{M^*}{M}\right)^{a+1} = (1-S)^{a+1} \quad (10)$$

We can also represent the reduction in molecular dimensions by means of the chain-branching index

$$g' \equiv \frac{[\eta]}{[\eta]_{lin}} \quad (11)$$

which with branching exclusively of the short chain type takes the value

$$g' = (1-S)^{a+1} \quad (12)$$

For practical cases, the formula derived by Stockmayer<sup>8</sup> for unperturbed dimensions

$$g = (s+1)^{-1}[1 + s(1 - 2f + 2f^2 - 2f^3) + s^2(-f + 4f^2 - f^3)] \quad (13)$$

(with  $s$  = number of short side chains and  $f$  = mass fraction of each side chain) is approximated very closely by

$$g = 1 - sf = 1 - S \quad (14)$$

If  $sf \leq 0.1$  and  $s \geq 10$ , the deviation is smaller than 1%. The equations of Berry and Orofino<sup>9</sup> and Berry<sup>10</sup> for the dimensions of SCB macro-

molecules under theta conditions are equally well approximated by

$$g = 1 - S$$

as also follows from the calculations by Schröder and Winkler.<sup>11</sup> This equality of  $g$  and  $1 - S$  under theta conditions leads direct to  $M^*/M = 1 - S$  (because under these conditions the mean square radius of gyration is proportional of  $M$ ). If we assume the chain expansion occurring when a theta solvent is replaced by a good solvent to be a function of the chain dimensions (and not of the molar mass), it follows that  $M^*$  remains constant at this expansion, and that  $M^*/M = 1 - S$  also under non-theta conditions. This, as indicated above, leads to

$$g' = (1 - S)^{a+1} \quad (12)$$

On the above assumption, the following holds for virtually linear polyolefins with short chain branching only:

$$M^* = M(1 - S) \quad (9)$$

$$[\eta] = (1 - S)^{a+1} K_{PE} M^a \quad (15)$$

$$[\eta] = (1 - S) K_{PE} (M^*)^a \quad (16)$$

with  $S$  being the mass fraction of the short side chains.

For various polyolefins  $1 - S$  has the following values:

polyethylene	$1 - S = 1$	(17)
--------------	-------------	------

polypropylene	$1 - S = 2/3$	(18)
---------------	---------------	------

ethylene-propylene copolymer	$1 - S = 1 - \frac{1}{3} W_3$	(19)
---------------------------------	-------------------------------	------

( $W_3 =$  mass fraction of propylene)

ethylene-1-alkene copolymer	$1 - S = 1 - (1 - 2/n)W$	(20)
--------------------------------	--------------------------	------

( $W =$  mass fraction of 1-alkene;  
 $n =$  number of C atoms in 1-alkene)

With polydisperse polymers for which the fraction of short side chains, or the comonomer content, does not vary with the molar mass, eqs. (9), (15), and (16) hold for all components with the same value of  $S$ . Equation (9) then holds also for  $M_n$  and  $M_w$ , eqs. (15) and (16) for the  $[\eta]$  vs.  $M_v$  and  $[\eta]$  vs.  $M_v^*$  relations. From (10) and (15) also the equation given by Ambler<sup>22</sup> can be derived directly:

$$[\eta] = K^{1/(1+a)} \sum f_i ([\eta]_i M_i)^{a/(1+a)} \quad (21)$$

which equation enables, for instance, the  $K$  [in this particular case  $(1 - S)^{\alpha+1}K_{PE}$ ] of the polymer-solvent system to be determined from viscosity  $([\eta])$  and GPC  $([\eta], M_i)$  measurements.<sup>23</sup>

If  $S$  (or  $W$ ) varies with the molar mass, the above equations no longer apply with the  $S$  (or  $W$ ) of the whole polymer; then the influence of the portion having the higher molar mass prevails. In extreme cases, for instance, with a mixture of a short-chain branched polymer of high molar mass and an unbranched polymer of low molar mass, this has duly to be taken into account. With most copolymers used in practice the deviation can be neglected, however.

In the case of polymers having both long-chain and short-chain branching both types contribute to the reduction of the molecular dimensions. The branching index  $g'$ , defined by eq. (11), can then be written as<sup>6,7,21</sup>

$$g' = g'_{LCB} \cdot g'_{SCB} \quad (22)$$

For commercial LDPEs the value of  $g'_{SCB}$  is mostly of the order of 0.85. If so desired, the experimentally determined  $g'$  can be corrected for the influence of short-chain branching in determination of the degree of long-chain branching.

### COMPARISON WITH EXPERIMENTAL DATA FROM LITERATURE

Very good experimental data are contained in the publications by Arnett and Stacy.<sup>17,24</sup> These concern the mean molar masses  $M_w$  and  $M_n$  and the intrinsic viscosities in six different solvents of hydrogenated polybutadienes with four degrees of 1,2 addition (which results in formation of an ethyl side chain), and a series of molar masses for each composition.

From these data we calculated the constants of the Mark-Houwink equations ( $K_x$  represents the Mark-Houwink constant for a polyolefin with  $x$  ethyl side chains per 1000 C atoms; for all polymers the same exponent  $a$  has been assumed for a given solvent) (see Table I). For these calculations  $M$  is expressed as number of moles per gram and  $[\eta]$  as number of demiliters per gram. From data by Wagner and Hoeve<sup>25</sup> for polyethylene in 1-chloronaphthalene ( $[\eta] = 5.55 \times 10^{-4} M^{0.684}$ ) we calculated, for  $a = 0.68$ , the value  $K = 5.8 \times 10^{-4}$ . To test eq. (10),  $K/K_{PE} = (1 - S)^{\alpha+1}$ , for correctness, we can calculate from the experimental values the quotient  $[K_x/K_y]^{1/(\alpha+1)}$  and compare it with  $(1 - S_x)/(1 - S_y)$  (see Table II). From these data it can be inferred that, within the usual accuracy of measurement, eqs. (9) and (10) may be used. Also experiments carried out by Schröder and Winkler<sup>12</sup> show that these equations are reasonably satisfactory.

### EXPERIMENTAL

Intrinsic viscosity measurements were performed with an Ubbelohde capillary viscometer. Because of relatively long flow times the correction for kinetic energy could be ignored. The samples were dissolved in the viscometer reservoir at 135°C, and the solutions were diluted by adding fresh solvent. Weight average molar masses were determined by light-scattering photometry, using a Sofica 42000 Apparatus and 1-chloronaphthalene as

TABLE I

Temp (°C)	Solvent	$\alpha$	$10^4 \times K_{19}$	$10^4 \times K_{89}$	$10^4 \times K_{130}$	$10^4 \times K_{183}$
35	2,4-Dimethylpentane (4)	0.66		5.72	4.56	3.65
35	Heptane (5)	0.70		4.24	3.20	2.54
35	Cyclohexane (6)	0.72		4.20	3.18	2.50
130	Dodecanol (1)	0.62	7.15	6.06	4.55	3.68
130	Biphenyl (2)	0.64	6.28	5.55	3.81	2.84
130	1-Chloronaphthalene (3)	0.68	5.28	4.59	3.33	2.41

TABLE II

	For solution in solvent	$x = 130$	$x = 183$	
Experimental $(K_x/K_{69})^{1/(1+a)}$	4	0.87	0.76	
	5	0.85	0.74	
	6	0.85	0.74	
	Average	0.86	0.75	
Compare with $(1 - S_x)/(1 - S_{69})$		0.86	0.74	

	For solution in solvent	$x = 69$	$x = 130$	$x = 183$
Experimental $(K_x/K_{19})^{1/(1+a)}$	1	0.90	0.76	0.66
	2	0.93	0.74	0.62
	3	0.92	0.76	0.63
	Average	0.92	0.75	0.64
Compare with $(1 - S_x)/(1 - S_{19})$		0.90	0.77	0.66

	For solution in 1-chloronaphthalene			
	$x = 19$	$x = 69$	$x = 130$	$x = 183$
Experimental $(K_x/K_{PE})^{1/(1+a)}$	0.94	0.87	0.72	0.59
Compare with $(1 - S)$	0.96	0.86	0.74	0.63

solvent. The samples were dissolved at 150°C for 4 h, filtered over a 1.2- $\mu\text{m}$  silver filter and measured at 140°C. Refractive index increments values of 0.189 were used for all polyolefines.

Number average molar masses were determined with a Knauer membrane osmometer in 1,2,4-trichlorobenzene (TCB) at 125°C with use of Ultracella "allerfeinst" membranes (Sartorius, Göttingen).

GPC measurements were performed with a Waters Model 200 instrument with TCB at 135°C and four columns packed with styragel ( $10^3$ - $10^4$ - $10^5$ - $10^6$  Å). The instrument was calibrated with rather narrow PE samples of known  $M_n$  and  $M_w$ , which provided the apparent molar masses  $M_n^*$ ,  $M_w^*$  and  $M_z^*$ .

### DATA ON LINEAR POLYETHYLENE

Literature contains very numerous data on the relation between intrinsic viscosity and molar mass for the most used solvents. However, there is a large spread in the value of the Mark-Houwink exponent  $a$  and hence also in the value of the constant  $K$ .<sup>26,27</sup> Our own research on linear polyethylene, whole polymers as well as rather narrow fractions, with application of the correction for the width of the molar weight distribution as indicated above, and comparison with the best values from literature resulted in the following Mark-Houwink equations:

$$[\eta] = 4.75 \times 10^{-4} M^{0.725} \quad \text{for PE in decalin at 135°C} \quad (23)$$

and

$$[\eta] = 4.06 \times 10^{-4} M^{0.725} \quad \text{for PE in TCB at 135°C} \quad (24)$$



Because decalin is an even better polyethylene solvent than TCB, the exponent  $a$  might be expected to have a slightly higher value for decalin. The difference is within the experimental error, however. We also found a nearly constant ratio (1.17) between the intrinsic viscosities in decalin and TCB, for HDPE as well as LDPE and LLDPE samples (Christensen<sup>28</sup> found the same ratio for the NBS standard sample SRM 1475). With the less good solvent 1-chloronaphthalene Wagner and Hoeve<sup>25</sup> found a distinctly lower exponent ( $a = 0.684$ ).

### DATA ON LINEAR POLYPROPYLENE

Of a series of standard samples of linear polypropylene acquired from the National Physical Laboratory (NPL) at Teddington, U.K., we measured the intrinsic viscosities in decalin and TCB.  $M_w$  values were determined direct by means of the SOFICA and the Chromatix KMX-6 equipment as well as by GPC, using the KMX-6 on-line. From the results of these measurements, the  $[\eta]$  values found, and the  $M_w$  values given by NPL,<sup>29</sup> we found the following average values of the Mark-Houwink constants:

$$K = 2.38 \times 10^{-4}, \quad a = 0.725 \quad \text{for PP in decalin at } 135^\circ\text{C}$$

and

$$K = 1.90 \times 10^{-4}, \quad a = 0.725 \quad \text{for PP in TCB at } 135^\circ\text{C}$$

The intrinsic viscosities in decalin or TCB of six linear polypropylene homopolymer samples and a large number of fractions of these samples were also measured, and gel permeation chromatograms (in TCB) for the same substances were prepared to determine  $M_w^*$  and  $M_n^*$  values. We thus arrived at the following relation:

$$[\eta] = 2.64 \times 10^{-4} (M^*)^{0.725} \quad \text{for PP in TCB at } 135^\circ\text{C} \quad (25)$$

Combining this relation with the Mark-Houwink equation for polyethylene in TCB, one gets

$$K = 1.93 \times 10^4 \text{ for PP in TCB at } 135^\circ\text{C}$$

According to eq. (5) the  $M^*$  value determined for linear polypropylene by GPC can be converted to the absolute molar mass  $M$ . The fact that the Mark-Houwink exponents  $a$  for polyethylene and polypropylene are equal (both being 0.725) makes this conversion amount to a multiplication by the constant factor  $(4.06 \times 10^{-4} / 1.90 \times 10^{-4})^{1/1.725} = 1.55$ . Within the accuracy of measurement this factor is equal to the theoretical factor 3/2. Also with polypropylene we found a constant ratio between the intrinsic viscosities in decalin and TCB (at 135°C), viz. 1.25, which is different from the ratio for polyethylene.

This difference in the ratios between  $[\eta]$  in decalin and  $[\eta]$  in TCB is not in accordance with what one would expect from eq. (10) [and eq. (15)], as both  $S$  and  $a$  may here be regarded as constants. We have the impression

that polypropylene in decalin (the best solvent) satisfies the presupposition of eqs. (9) and (10) best; here  $K_{PP}/K_{PE} = 0.50$ , which is very close to  $(2/3)^{1.725}$ .

### ETHYLENE-PROPYLENE COPOLYMERS

With use of a catalyst system consisting of an aluminium alkyl combined with a vanadium component as transition metal,<sup>30</sup> a few series of linear ethylene-propylene copolymers differing in composition and molar mass were prepared. Figure 1 gives a survey of the samples produced, indicating the propylene contents and the apparent molar masses ( $M_w^*$ ). The catalyst system did not allow high molar mass values to be obtained with high propylene contents: In the three samples having the highest  $C_3$  percentage,  $M_w^*$  remained below 20 kg/mol. The propylene contents of these samples were determined by <sup>13</sup>C-NMR and in some cases by IR spectroscopy. No data concerning the compositional fluctuation within the samples are known; these will be determined in due time. We further measured the intrinsic viscosities (in decalin at 135°C, and, for some samples, in TCB at 135°C), the GPC molar mass distributions, with  $M_n^*$ ,  $M_w^*$ , and  $M_z^*$ , on the basis of calibration with linear polyethylene, the number-average molar masses (by vapor-phase and membrane osmometry), and—for some samples—the weight-average molar masses (by light scattering). Table III lists the samples and the results of the measurements. As an example, Figure 2 gives the GPC molar mass distributions of two samples plotted vs.  $\log M^*$ , that is, the GPC molar mass calculated on the basis of calibration with linear polyethylene. In order to test eq. (9) (with  $S = 1 - \frac{1}{3}W_3$  for EP copolymer), we have plotted the  $M_w^*/M_w$  ratio vs.  $W_3$  (see Fig. 3). Almost none of the points deviates by more than 15% (which is about equal to the sum of the measuring accuracies for  $M_w$  and  $M_w^*$ ) from the straight line  $f(W) = 1 - \frac{1}{3}W_3$ . However, as the effect to be measured is not much greater

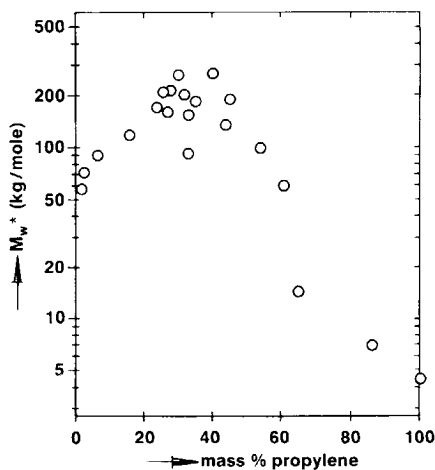


Fig. 1. Composition and molar mass of the ethylene-propylene copolymers.

TABLE III  
 Propylene Content, Intrinsic Viscosities, and Average Molar Masses of the Ethylene-Propylene Copolymers<sup>a</sup>

Sample	100 $W_3$	$[\eta]_{dec}^{135}$	$[\eta]_{dec}^{135}$	$[\eta]_{RCB}^{35}$	$\frac{[\eta]_{dec}^{135}}{[\eta]_{RCB}^{35}}$	$M_n$	$M_w$	$M_n^*$	$M_w^*$	$M_z^*$
EJU 191	100	0.14				1.85		1.0	45	73
EJU 192	86	0.20				2.9		1.9	7	
EJU 193	64	0.37						5.7	15.4	26
EJU 195	61	1.05		0.87	1.21	32	68	27	61	110
EJU 196	54	1.51/1.54		1.23	1.24	41	120	40	98	182
EJU 155	44	1.90		1.59	1.19	54	165	57	133	240
EJU 197	45	2.40		2.04	1.18	80	190	78	190	350
EJU 198	40	3.15		2.75	1.15	120	290	105	270	470
EJU 159	35	2.50				71		78	184	320
EJU 215	30	3.41		2.90	1.18	87	310	110	266	440
EJU 213	33	2.21				67/60		62	153	270
EJU 212	33	1.48		1.29	1.15	42	110	41	91	160
EJU 199	32	2.86				74		76	200	350
EJU 200	28	2.86				66		67	215	380
EJU 201	26	2.74		2.26	1.21	59	210	62	207	370
EJU 202	27	2.39				46		56	159	300
EJU 203	24	2.56		2.15	1.19	52/50	200	25	170	320
EJ 207	16	1.97				42		39	120	220
EJ 208	6.6	1.57		1.39	1.13	32	100	41	91	160
EJ 210	2.4	1.26				28		28	72	130
EJ 211	1.7	1.16				25		25	58	100

<sup>a</sup> All  $[\eta]$  in dl/g, all  $M$  in kg/mol.

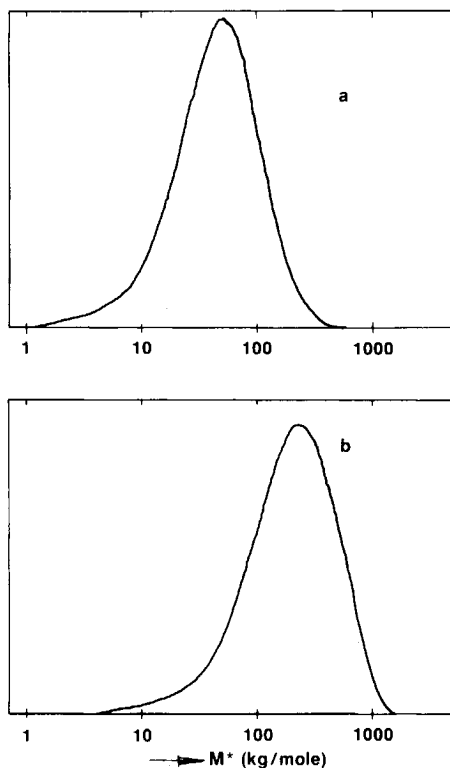


Fig. 2. Apparent molar mass distribution (GPC) (a) of sample EJU 195 and (b) of sample EJU 215.

than the accuracy of measurement, this graph is hardly significant. A more accurate comparison can be made by starting from  $[\eta]$  and  $M_w$  or from  $[\eta]$  and  $M_w^*$ .

According to eqs. (15), (16), and (19), these ethylene-propylene copolymers should satisfy the following relations:

$$[\eta] = \left(1 - \frac{1}{3}W_3\right)^{a+1} K_{PE} M_w^a \quad (26)$$

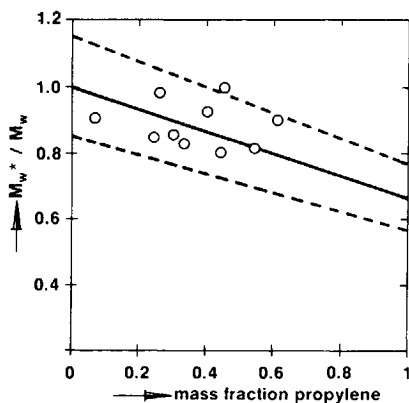


Fig. 3. Ratio  $M_w^*/M_w$  of EP copolymers as a function of mass fraction propylene ( $W_3$ ).

TABLE IV  
Calculated Data for the Ethylene-Propylene Copolymers

Sample	$M_v$	$M^*$	$\frac{[\eta]_{dec}^{0.85}}{K_{PE}M_v^{0.725}}$	$\frac{[\eta]_{dec}^{0.85}}{W_3^{-1.725}} \times (1 - 1/3)^{-1}$	$\frac{[\eta]_{dec}^{0.85}}{K_{PE}M_v^{0.725}}$	$\frac{[\eta]_{dec}^{0.85}}{W_3^{-1.725}} \times (1 - 1/3)^{-1}$	$\frac{[\eta]_{dec}^{0.85}}{K_{PE}M_v^{0.725}}$	$\frac{[\eta]_{dec}^{0.85}}{W_3^{-1.725}} \times (1 - 1/3)^{-1}$	$\frac{[\eta]_{dec}^{0.85}}{K_{PE}M_v^{0.725}}$	$\frac{[\eta]_{dec}^{0.85}}{W_3^{-1.725}} \times (1 - 1/3)^{-1}$
EJU 191		3.66	0.77	0.21	0.77	0.21				
192		6.2	0.75	0.28	0.75	0.28				
193		13.4	0.79	0.47	0.79	0.47				
195	61.3	54.5	0.81	1.32	0.81	1.32	0.72	1.29	0.78	1.09
196	103.5	86.6	0.84	1.86	0.84	1.86	0.69	1.73	0.79	1.50
155	141.5	118.4	0.74	2.15	0.74	2.15	0.72	2.09	0.81	1.86
197	168.7	168.1	0.82	2.50	0.82	2.50	0.81	2.70	0.81	2.40
198	256.9	237.1	0.82	3.18	0.82	3.18	0.80	3.52	0.85	3.17
159	163.5		0.84	4.03	0.84	4.03	0.87			
215	260.3	235.6	0.87	2.83	0.87	2.83	0.84	3.48	0.90	3.22
213	135.1		0.91	4.09	0.91	4.09	0.89	2.48		
212	96.4	81.6	0.89	1.81	0.89	1.81	0.86	1.58	0.86	1.45
199	175.1		0.86		0.86		0.95	3.20		
EJU 200		183.2	0.92		0.92		0.92	3.15		
201	176.4	175.4	0.91	3.20	0.91	3.20	0.87	2.64	0.87	2.47
202	137.8		0.95		0.95		0.95	2.63		
203	165.7	154	0.93	2.96	0.93	2.96	0.86	2.48	0.91	2.34
EJ 207		102.8	0.96		0.96		0.96	2.08		
208	85.5	81.6	0.91	1.63	0.91	1.63	0.90	1.44	0.93	1.42
210		63.2	0.88		0.88		0.88	1.27		
211		51.7	0.93		0.93		0.93	1.17		

\* M in kg/mol,  $[\eta]$  in dL/g.

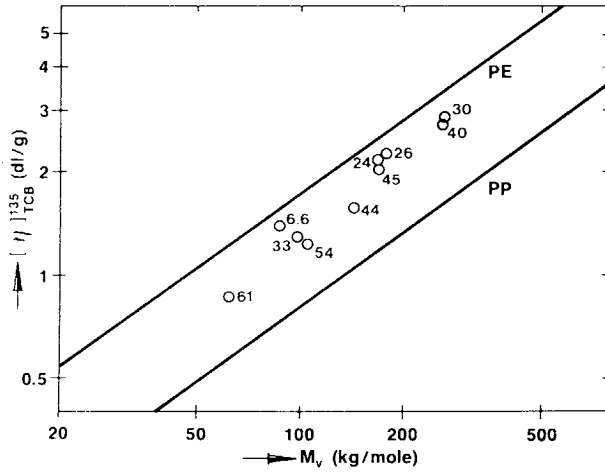


Fig. 4.  $[\eta]_{\text{TCB}}^{135}$  vs.  $M_v$  for EP copolymers (mass % propylene is indicated near the points): (—) Mark-Houwink equations for polyethylene and polypropylene in TCB.

and

$$[\eta] = \left(1 - \frac{1}{3}W_3\right)K_{\text{PE}}(M^*_v)^a \quad (27)$$

with  $a = 0.725$  and  $K_{\text{PE}} = 4.75 \times 10^{-4}$  for decalin and  $K_{\text{PE}} = 4.06 \times 10^{-4}$  for TCB.

Table IV shows a number of values calculated from the measurements data;  $M_v$  and  $M^*_v$  were calculated with the use of eq. (7). For the samples EJU 192 and EJU 203, which have GPC distributions that are far from log-normal,  $M^*_v$  was calculated from  $[\eta]^*$  (GPC) according to the Mark-Houwink equation for polyethylene in TCB.

Figure 4 shows the intrinsic viscosity in TCB as a function of  $M_v$  for the samples whose  $M_w$  values were measured. Also shown in this graph are the

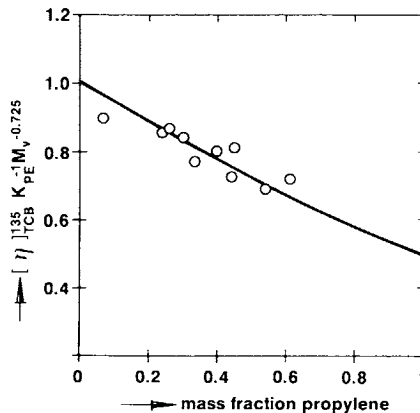


Fig. 5. Ratio  $[\eta]_{\text{TCB}}^{135} / K_{\text{PE}} M_v^{0.725}$  as a function of mass fraction propylene: (—) theoretical value  $f(W_3) = \left(1 - \frac{1}{3}W_3\right)^{1.725}$ .

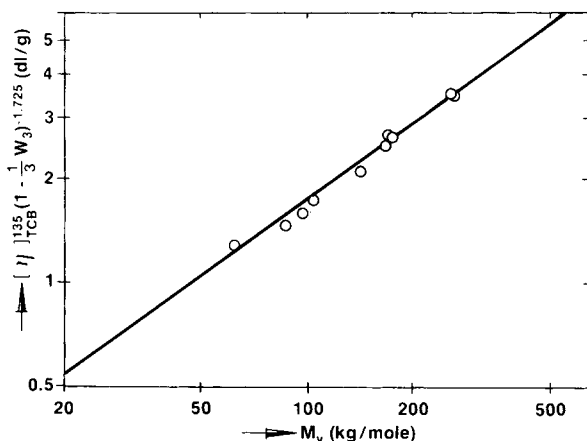


Fig. 6.  $[\eta]_{\text{TCB}}^{135} (1 - \frac{1}{3} W_3)^{-1.725}$  as a function of  $M_v$ : (—) Mark-Houwink equation for polyethylene in TCB.

lines representing the Mark-Houwink equations for polyethylene and polypropylene. It is seen that the points lie within the space between these lines, proportionally to the mass fraction of propylene contained in the samples with a spread that is smaller than the accuracy of measurement. This is made clear by Figure 5, in which

$$[\eta]_{\text{TCB}}^{135} / [K_{\text{PE}} M_v^{0.725}]$$

has been plotted as a function of the mass fraction of propylene,  $W_3$ . Within the accuracy of measurement ( $\sim 10\%$ ), all points lie on the line given by (1) —  $\frac{1}{3} W_3^{1.725} = f(W_3)$ .

If we plot

$$[\eta]_{\text{TCB}}^{135} (1 - \frac{1}{3} W_3)^{-1.725}$$

vs.  $M_v$  (Fig. 6), it is seen that within the accuracy of measurement all points lie on the line representing the Mark-Houwink equation for polyethylene in TCB.

For these samples Figure 7 gives the intrinsic viscosity in TCB as a function of  $M_v^*$ . The line for the Mark-Houwink equation for polyethylene and that for the  $[\eta]$  vs.  $M^*$  relation for polypropylene according to eq. (25) are shown also in this graph.

Figure 8 shows

$$[\eta]_{\text{TCB}}^{135} / [K_{\text{PE}} (M_v^*)^{0.725}]$$

as a function of  $W_3$ . Almost all points are well on the line defined by the function  $(1 - \frac{1}{3} W_3) = f(W_3)$ .

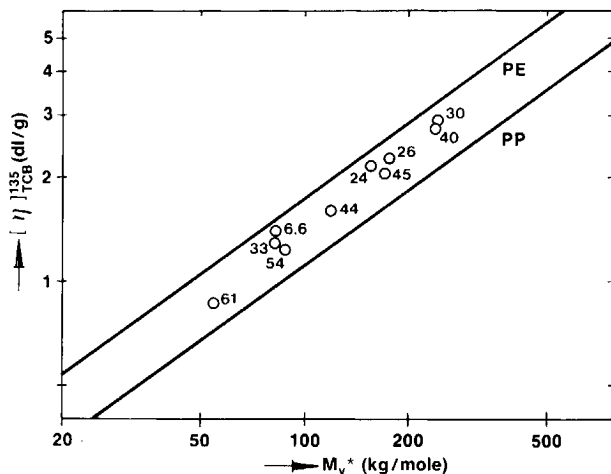


Fig. 7.  $[\eta]_{TCB}^{135}$  vs.  $M_v^*$  for EP copolymers (mass % propylene is indicated near the points): (—) Mark-Houwink equation for polyethylene and  $[\eta]_{TCB}^{135} - M_v^*$  relation for polypropylene in TCB.

A plot of

$$[\eta]_{TCB}^{135} \left(1 - \frac{1}{3} W_3\right)^{-1}$$

vs.  $M_v^*$  (Fig. 9) shows that, within the accuracy of measurement, all points lie on the straight line representing the Mark-Houwink equation of polyethylene.

Similar investigations are done on the relations of  $[\eta]$  in decalin to  $M$  and  $M^*$ , with comparable results. We give two examples. Figure 10 shows for all samples the intrinsic viscosity in decalin as a function of  $M_v^*$ . Again, the points lie between the lines for polyethylene and polypropylene, in positions determined by the propylene content. The values of

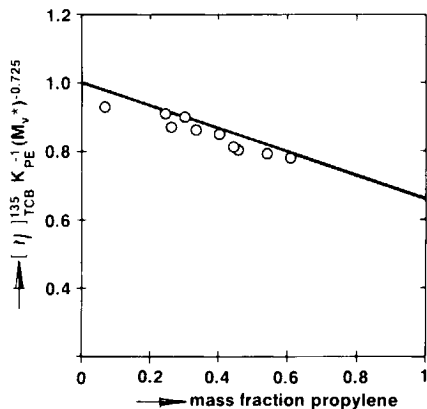


Fig. 8. Ratio  $[\eta]_{TCB}^{135} / K_{PE} (M_v^*)^{0.725}$  as a function of mass fraction propylene: (—) theoretical value  $f(W_3) = 1 - \frac{1}{3} W_3$ .



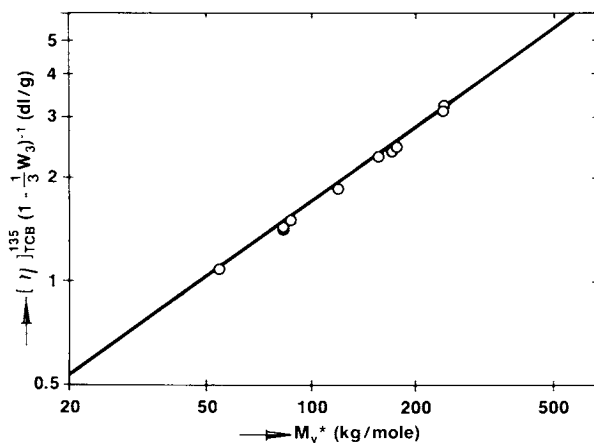


Fig. 9.  $[\eta]_{TCB}^{135} (1 - \frac{1}{3}W_3)^{-1}$  as a function of  $M_v^*$ : (—) Mark-Houwink equation for polyethylene in TCB.

$$[\eta]_{dec}^{135} (1 - \frac{1}{3}W_3)^{-1}$$

plotted vs.  $M_v^*$  prove to be well represented by the Mark-Houwink equation for polyethylene (Fig. 11).

What has been said above shows that, within the normal accuracies of measurement, eqs. (26) and (27) hold for linear ethylene-propylene copoly-

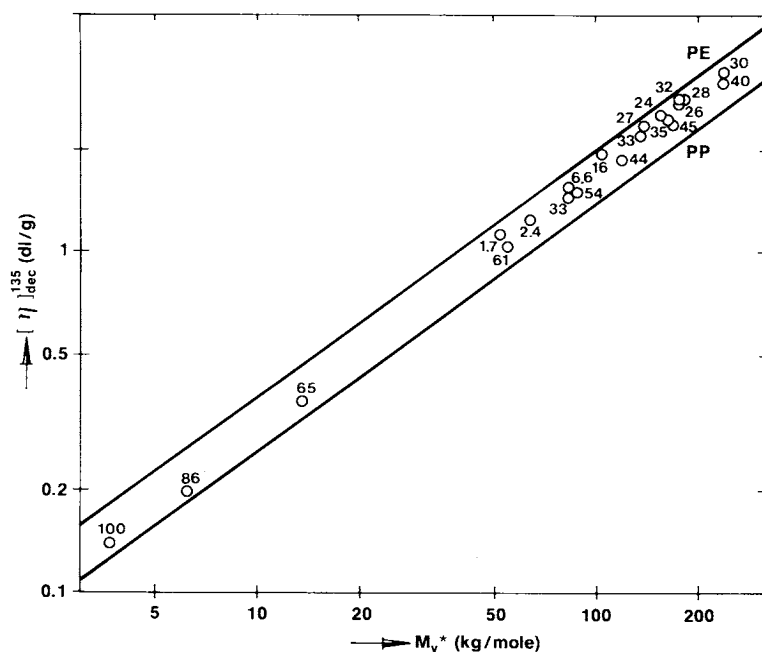


Fig. 10.  $[\eta]_{dec}^{135}$  vs.  $M_v^*$  for all EP copolymers (mass % propylene is indicated near the points): (—) Mark-Houwink equation for polyethylene and  $[\eta]_{dec}^{135} - M_v^*$  relation for polypropylene in decalin.

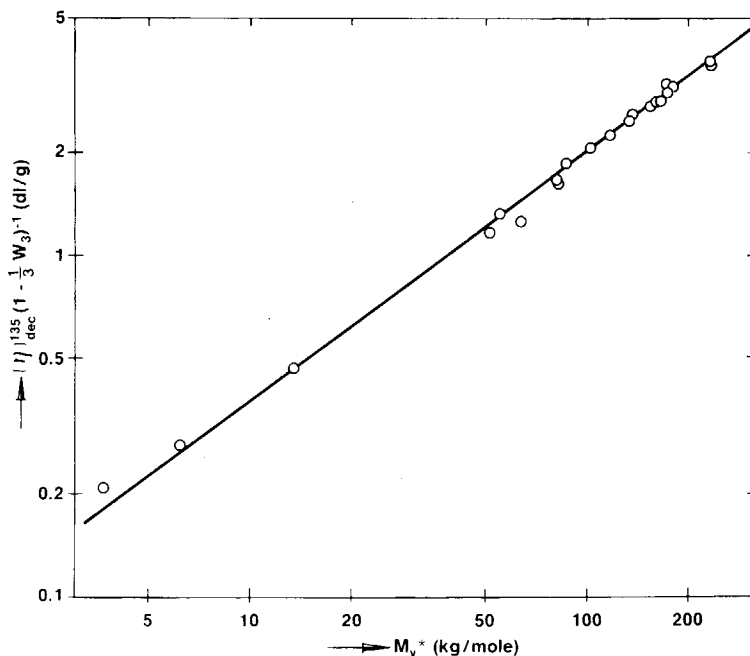


Fig. 11.  $[\eta]_{\text{dec}}^{135} (1 - \frac{1}{3} W_3)^{-1}$  as a function of  $M_v^*$ : (—) Mark-Houwink equation for polyethylene in decalin.

mers, which means that the simple principle expressed by eqs. (9), (10), and (12) applies here, too. This implies that  $M^*$  values calculated from results from GPC calibrated with linear polyethylene can be converted directly to the correct molar masses by multiplication by the factor  $(1 - \frac{1}{3} W_3)^{-1}$  (that is to say, for uniform propylene content) and that, in determining the degree of long-chain branching, the influence of short-chain branching can be eliminated by dividing  $g'$  by  $(1 - \frac{1}{3} W_3)^{1+a}$ . The often-used method of deriving,

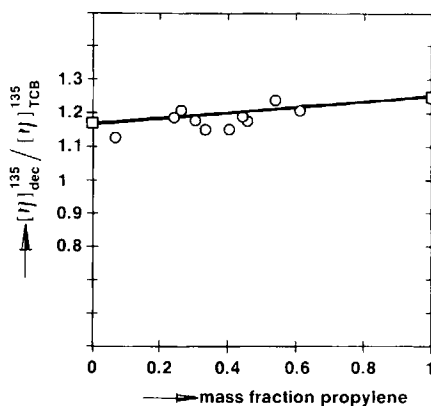


Fig. 12. Ratio  $[\eta]_{\text{dec}}^{135} / [\eta]_{\text{TCB}}^{135}$  for polyethylene, polypropylene, and ethylene-propylene copolymers as a function of mass fraction propylene.

for a given exponent  $a$ , the  $K$  values of ethylene-propylene copolymers from  $K$ s of the two homopolymers by linear interpolation (applied to mass fractions)<sup>27,31,32</sup> does not differ much from the use of eqs. (10) and (19).

As Figure 5 shows for the experimentally determined  $K$  values, the deviation from a linear relationship with the mass composition is within the accuracy of measurement. The relation given by Ogawa and Inaba,<sup>33</sup> however, is completely different in this respect. The equations of Wang et al.<sup>34</sup> for EP copolymers in ODCB gives a somewhat greater decrease of  $K$  with the propylene content.

For the ratio between the intrinsic viscosities in decalin and TCB we found the factors 1.17 for polyethylene (with linear model samples as well as with HDPE and LDPE) and 1.25 for polypropylene.

If for the 10 ethylene-propylene samples for which both  $[\eta]_{\text{dec}}^{135}$  and  $[\eta]_{\text{TCB}}^{135}$  were measured this ratio is plotted as a function of the propylene mass fraction, it is seen to increase with  $W_3$  and to be represented, within the accuracy of measurement, by a straight line (Fig. 12). Consequently, we can use as conversion factor in this case

$$[\eta]_{\text{dec}}^{135} / [\eta]_{\text{TCB}}^{135} = 1.17 + 0.08 W_3$$

The authors are indebted to Mrs. J. van den Bosch and R. Graff who prepared the copolymer samples (on request of Dr. V. Mathot) and to Mr. A. Veermans for the NMR and IR analyses. They also thank Dr. C. J. Stacey (Bartlesville, United States) for furnishing the original molar mass and intrinsic viscosity data of Ref. 17.

## References

1. A. C. Ouano, *J. Chromatogr.*, **118**, 303 (1976).
2. B. Millaud and C. Strazielle, *Makromol. Chem.*, **180**, 441 (1979).
3. R. Prechner, R. Panaris, and H. Benoit, *Makromol. Chem.*, **156**, 39 (1972).
4. Th. G. Scholte and N. L. J. Meijerink, *Br. Polym. J.*, **9**, 133 (1977).
5. B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).
6. J. E. Guillet, *J. Polymer Sci. A*, **1**, 2869 (1963).
7. E. Schröder, *Plaste Kautschuk*, **20**, 241 (1973).
8. See F. W. Billmeyer, *J. Am. Chem. Soc.*, **75**, 6118 (1953).
9. G. C. Berry and T. A. Orofino, *J. Chem. Phys.*, **40**, 1614 (1964).
10. G. C. Berry, *J. Polym. Sci., A-2*, **6**, 1551 (1968).
11. E. Schröder and E. Winkler, *Plaste Kautschuk*, **21**, 269 (1974).
12. E. Schröder and E. Winkler, *Plaste Kautschuk*, **21**, 910 (1974).
13. G. Popov, K. Gehrke and J. Ulbricht, *Plaste Kautschuk*, **21**, 515 (1974).
14. P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).
15. H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York, 1971.
16. W. H. Stockmayer and M. Fixman, *Ann. N.Y. Acad. Sci.*, **57**, 334 (1953).
17. R. L. Arnett and C. J. Stacy, *J. Phys. Chem.*, **77**, 1986 (1973).
18. M. Bohdanecky and J. Kovár, *Viscosity of Polymer Solutions*, North-Holland, Amsterdam, 1982.
19. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci., B*, **5**, 753 (1967).
20. R. Koningsveld and C. A. F. Tuijnman, *Makromol. Chem.*, **38**, 39 (1960).
21. Th. G. Scholte, in *Developments in Polymer Characterisation—4*, J. V. Dawkins, Ed., Applied Science, Barking, 1983.
22. M. R. Ambler, *J. Polym. Sci. (Pol. Chem. Ed.)*, **11**, 191 (1973).
23. B. Iván, Z. Laszlo-Hedvig, T. Kelen, and F. Tüdös, *Polym. Bull.*, **8**, 311 (1982).
24. C. J. Stacy and R. L. Arnett, *J. Phys. Chem.*, **77**, 78 (1973).
25. H. L. Wagner and C. A. J. Hoeve, *J. Polym. Sci. (Pol. Phys. Ed.)*, **11**, 1189 (1973).

26. F. B. Baldwin and G. Ver Strate, *Rubber Chem. Technol.*, **45**, 709 (1972).
27. C. Strazielle, *Pure Appl. Chem.*, **42**, 615 (1975).
28. R. Christensen, *J. Res. Natl. Bur. Std., A*, **76A**, 147 (1972).
29. C. M. L. Atkinson and R. Dietz, *Makromol. Chem.*, **177**, 213 (1976).
30. V. Mathot, M. Pijpers, J. Beulen, R. Graff, and G. van der Velden, *Proceedings of the Second European Symposium on Thermal Analysis*, Heyden, London, 1981, p. 264.
31. G. Moraglio, *Chem. Ind. (Milan)*, **10**, 984 (1959).
32. D. W. van Krevelen and P. J. Hoftijzer, *J. Appl. Polym. Sci.*, **10**, 133 (1966).
33. T. Ogawa and T. Inaba, *J. Appl. Polym. Sci.*, **21**, 2979 (1977).
34. Ke-Qiang Wang, Shi-Yu Zhang, Jia Xu, and Yang Li, *J. Liquid Chromatogr.*, **5**, 1899 (1982).

Received November 8, 1983

Accepted March 13, 1984