

On the Q-Factors for Poly-1-Olefins in Gel Permeation Chromatography

SADAO MORI, *Laboratory of Chemistry, Faculty of Engineering, Yamanashi University, Kofu, 400, Japan*

Synopsis

The Q-factors for ten poly-1-olefins from poly-1-butene to poly-1-octadecene were determined in 1,2,4-trichlorobenzene at 80°C and 135°C using the universal calibration curve and the elution count-extended chain length calibration curve constructed by use of polystyrene standards. These experimentally determined Q-factors were lower than the theoretical ones, except for poly-1-butene, at both temperatures, in contrast to those for polyethylene, polypropylene, and poly-1-butene. Corrected Q-factors for poly-1-olefins were obtained by correlating apparent Q-factors with the number of carbon atoms in the monomer for a series of poly-1-olefins. By assuming that poly-1-olefins in solution exist as quasi-rod-shaped polymers rather than random coils, it would be presumed that the apparent extended chain lengths of poly-1-olefins experimentally determined are longer than the theoretical ones because of the effects of their long pendent groups which influence the elution positions of poly-1-olefins. A molecule of the poly-1-olefins having the same theoretical extended chain length of a polystyrene molecule elutes earlier than the polystyrene molecule, meaning the extended chain length of the poly-1-olefin molecule is supposed to be longer than that of the polystyrene molecule.

INTRODUCTION

The measurement of molecular weight averages and the distributions for polymers by GPC requires the construction of a calibration curve. Relatively monodisperse polymers whose average molecular weights (or molecular size) are known are preferable as standard samples to construction of the calibration curve, and a series of polystyrenes in the molecular weight range of 10^3 – 10^6 with $\bar{M}_w/\bar{M}_n < 1.15$ is generally used for the calibration of a system of chromatographic columns for a given solvent at a specified temperature. Several relationships such as elution counts versus log MW, elution counts versus log extended chain length, and elution counts versus log (intrinsic viscosity \times MW) are applied for the construction of a calibration curve. The latter relationship is well known as a universal calibration curve,¹ and it is useful in the respect that the same calibration curve is used regardless of molecular species or the structures of polymers. However, in order to calculate the average molecular weight and the distribution for any polymer by using this universal calibration curve, it is required to trans-

form $[\eta]M$ units in the universal calibration curve to molecular weight units for the polymer specified for which Mark-Houwink coefficients in the same solvent at the same temperature to GPC were known, or to determine intrinsic viscosities of each fraction of GPC of the polymer. Further, fractionation and subsequent characterization are costly and time consuming. Therefore, the application of a universal calibration curve to the measurement of molecular weight distributions of polymers is not simple unless Mark-Houwink coefficients of the polymer over the entire range of molecular weights in the same operational conditions to GPC are known. In consequence, a procedure which uses the calibration parameter named Q-factor would still enhance the utility of GPC. In the procedure, weight- and number-average extended chain lengths are first calculated by use of the elution count-extended chain length curve for polystyrene standards, and then molecular weight averages are obtained as the products of extended chain length averages and the Q-factors of the polymers determined. The Q-factor is the ratio of molecular weight to the extended chain length calculated from bond lengths and valence angles.

A polymer-type independent relationship between elution volumes and the equivalent hydrogen radii of the polymer molecules has been demonstrated.² The hydrodynamic radii, however, are dependent on temperature or solvent.² Furthermore, the ratio of the extended chain length to the hydrodynamic radius varies with molecular weight of the polymer even in the same solvent and at the same temperature.³ The theoretical Q-factors for polyethylene and polypropylene, 11 and 17, calculated from bond lengths and valence angles, were supposed to be insufficient and the values, 17-17.3 for polyethylene³ and 26.4 for polypropylene,⁴ were reported as appropriate values by comparing molecular weight averages calculated from GPC data by this method with those obtained by classical (absolute) methods. Differences between GPC and classical averages of as much as 100% have been found. These differences appear to be too large to be explained by efficiency or operational variable effects. It is preferable, therefore, to determine the Q-factors experimentally in advance in the same solvent at the same temperature by using the standard polymer samples concerned.

This communication reports the results of the measurement of Q-factors for a series of poly-1-olefins in 1,2,4-trichlorobenzene at 80°C and 135°C, where the calculation of the Q-factors has been tried by using the universal calibration curve and the elution count-extended chain length calibration curve for polystyrene standards. Though some of poly-1-olefins employed here have broad distributions, it was assumed that a semilog plot of the product of intrinsic viscosity and peak molecular weight for a poly-1-olefin against its elution count coincided with the universal calibration curve which was constructed from a series of polystyrene standards. The different average extended chain lengths for the same poly-1-olefin were obtained at both temperatures, implying the necessity for using different Q-factors at different temperatures.

EXPERIMENTAL

A Waters gel permeation chromatograph Model 200 with a differential refractometer detector was used. The column arrangement consists of four columns in series with permeability limits designated as 10^6 , 10^5 , 8.5×10^3 , and 10^3 Å. Either 1,2,4-trichlorobenzene (TCB) or tetrahydrofuran (THF) was employed as solvents in the studies reported in this paper. Column oven was maintained at 80°C (system A) and at 135°C for TCB and at room temperature for THF (system C). A flow rate of 1.0 ml/min was maintained, and 2.0 ml of 0.1% (w/v) polymer solution was added following filtration under pressure. TCB includes 0.1% Ionol as an antioxidant. A nitrogen purge was used with the GPC to minimize oxidation reaction of solvent.

In making the appropriate elution count-extended chain length calibration curve, the elution count of a standard polystyrene was plotted versus its log peak extended chain length. Three calibration curves were obtained by determining GPC for polystyrene standards in TCB at 80°C and 135°C and in THF at room temperature, respectively. Calculation of the weight- and the number-average extended chain lengths for poly-1-olefins from GPC elution curves were performed by the usual procedure by quartering each count (5 ml) of the chromatograms determined and by measuring the height at each point. Determination of GPC elution curves was made two times for each polymer, and average values were obtained.

The universal calibration curve in TCB at 80°C was constructed using polystyrene standards. Intrinsic viscosities for polystyrene standards and poly-1-olefins in TCB at 80°C were measured by using an Ubbelohde viscometer.⁵ Apparent Q-factors for poly-1-olefins in TCB at 80°C were calculated by measuring peak molecular weights (M_{GPC}) from the universal calibration curve and peak extended chain lengths (A_{GPC}) from the elution count-log extended chain length calibration curve, followed by dividing M_{GPC} by A_{GPC} . Peak molecular weight is defined as molecular weight at the maximum position of the chromatographic peak.

Polymer samples employed in the present investigation were polyethylene SRM 1475 (NBS), polystyrene NBS 706, and a series of poly-1-olefins⁵ (see Table I). Polystyrene standards used for calibration were purchased from Waters Associates, Inc.

RESULTS

The M_{GPC} , A_{GPC} , and apparent Q-factors obtained by dividing M_{GPC} by A_{GPC} for poly-1-olefins measured in TCB at 80°C are listed in Table I. These Q-factors for poly-1-olefins having larger numbers of carbon atoms in the monomer than poly-1-butene (poly-1-pentene was not examined) were lower than the theoretical ones (see Table II), in contrast to the values for polyethylene, polypropylene, and poly-1-butene. This reason is discussed in a later section.

TABLE I
Peak Molecular Weight (M_{GPC}), Peak Extended Chain Length (A_{GPC}), and Apparent Q-Factors for Poly-1-Olefins Measured in 1,2,4-Trichlorobenzene at 80°C

Polymer	M_{GPC}	A_{GPC}	Apparent Q-factor
Poly-1-butene	3.98×10^5	1.17×10^4	34.0
	3.7×10^5	1.06×10^4	34.8
Poly-1-hexene	1.1×10^4	3.95×10^2	27.9
	1.53×10^4	4.95×10^2	30.9
Poly-1-heptene	3.62×10^4	9.7×10^2	37.4
	3.62×10^4	9.7×10^2	37.4
Poly-1-octene	6.67×10^4	1.85×10^3	36.0
	6.67×10^4	1.85×10^3	36.0
Poly-1-nonene	2.42×10^5	6.4×10^3	37.8
	2.2×10^5	5.9×10^3	37.3
Poly-1-decene	6.39×10^5	1.40×10^4	45.5
	6.39×10^5	1.40×10^4	45.5
Poly-1-undecene	5.45×10^5	1.20×10^4	45.4
	6.0×10^5	1.23×10^4	48.8
Poly-1-tridecene	8.73×10^5	1.57×10^4	55.6
	5.86×10^5	1.23×10^4	47.8
Poly-1-hexadecene	7.54×10^5	1.40×10^4	53.8
	7.9×10^5	1.41×10^4	55.8
Poly-1-octadecene	8.35×10^5	1.30×10^4	64.2
	8.35×10^5	1.30×10^4	64.2

TABLE II
Corrected Q-Factors for Poly-1-Olefins in 1,2,4-Trichlorobenzene at 80°C and 135°C

Polymer	Theoretical Q-factor	Corrected Q-factor	
		80°C	135°C
Poly-1-butene (C ₄)	22	34.0	
Poly-1-hexene (C ₆)	33	30.5	
Poly-1-heptene (C ₇)	38.6	33.0	
Poly-1-octene (C ₈)	44.1	36.0	
Poly-1-nonene (C ₉)	49.7	38.5	49.0 (50.5) ^a
Poly-1-decene (C ₁₀)	55.2	41.0	54.5 (54.5) ^a
Poly-1-undecene (C ₁₁)	60.6	44.0	59.5 (58.5) ^a
Poly-1-tridecene (C ₁₃)	71.7	49.0	69.5 (68.0) ^a
Poly-1-hexadecene (C ₁₆)	88.3	57.0	
Poly-1-octadecene (C ₁₈)	99.2	63.0	95.5 (96.0) ^a

^a The values in parentheses are apparent Q-factors (see text).

By assuming that real Q-factors for poly-1-olefins are linearly related to the number of carbon atoms in the monomer, least-squares analysis of the data leads to one straight line which correlates apparent Q-factors with the number of carbon atoms in the monomer for a series of poly-1-olefins from poly-1-hexene to poly-1-octadecene. The corrected Q-factors shown in Table II were calculated from the linear function, except for the corrected Q-factor for poly-1-butene which was obtained by extrapolating the relation for polyethylene and polypropylene.

TABLE III
Weight- and Number-Average Extended Chain Lengths of Polyethylene, Poly-1-Olefins,
and Polystyrene Measured by GPC^a

Polymer	System A (TCB, 80°C)			System B (TCB, 135°C)			System C (THF, room temp.)		
	\bar{A}_w $\times 10^{-3}$	\bar{A}_n $\times 10^{-3}$	\bar{A}_w/\bar{A}_n	\bar{A}_w $\times 10^{-3}$	\bar{A}_n $\times 10^{-3}$	\bar{A}_w/\bar{A}_n	\bar{A}_w $\times 10^{-3}$	\bar{A}_n $\times 10^{-3}$	\bar{A}_w/\bar{A}_n
Poly-1-nonene	9.6	1.77	5.4	8.1	1.78	4.6			
Poly-1-decene	45.8	6.5	7.1	34.4	4.2	8.2			
Poly-1-undecene	28.0	8.7	3.2	21.0	6.0	3.5			
Poly-1-tridecene	53.0	4.8	11.0	38.2	3.2	11.9			
Poly-1-octadecene	42.5	3.4	12.5	26.3	2.9	9.1			
Polyethylene (SRM 1475)				3.00	1.22	2.46			
Polystyrene (NBS 706)	6.83	3.23	2.11	7.30	3.35	2.17	6.90	3.21	2.15

^a NBS Data. Polystyrene NBS 706: $\bar{M}_w = 2.88 \times 10^6$ ($\bar{A}_w = 7.0 \times 10^3$, $Q = 41.1$), $\bar{M}_n = 1.36 \times 10^6$ ($\bar{A}_n = 3.3 \times 10^3$), $\bar{M}_w/\bar{M}_n = 2.12$, polyethylene SRM 1475: $\bar{M}_w = 5.31 \times 10^4$, $\bar{M}_n = 1.83 \times 10^4$, $\bar{M}_w/\bar{M}_n = 2.90$.

Several corrected Q-factors for poly-1-olefins at 135°C were calculated as follows. First, the weight-average molecular weight, \bar{M}_w , was calculated by multiplying \bar{A}_w at system A in Table III by the corrected Q-factor of the polymer at 80°C in Table II. Second, the apparent Q-factor for the polymer at 135°C was calculated dividing \bar{M}_w thus obtained by \bar{A}_w at system B in Table III. These apparent Q-factors at 135°C are shown in parentheses in Table II. Finally, the corrected Q-factors were calculated by plotting the apparent Q-factors against the number of carbon atoms in the monomer for poly-1-olefins, followed by obtaining a straight line by use of the least-squares method.

Weight- and number-average extended chain lengths for poly-1-olefins from poly-1-nonene to poly-1-octadecene, polyethylene SRM 1475, and polystyrene NBS 706 at different temperature are shown in Table III. The reproducibility of the measurements of molecular weight by GPC is normally considered to be about 5–6% in deviation, indicating that the values for polystyrene NBS 706 in Table III coincide with each other within the experimental error.

The average extended chain lengths for poly-1-olefins at 135°C were 20–40% lower than those at 80°C. As the values for polystyrene NBS 706 were unchanged, it seems to be too large to explain this difference for poly-1-olefins by the calibration error, and it might indicate a lack of constancy of the ratio of the extended chain lengths for both polystyrene and poly-1-olefin at both temperatures. Hydrodynamic radius, which is directly related to the GPC separation, varies with changing temperatures, and the rate of variation for poly-1-olefin supposedly does not equal that for polystyrene. This means that comparison of the extended chain lengths of polymers obtained at different temperatures is meaningless if the calibration

curve is constructed from different types of polymers such as polystyrene in this case and that the Q -factors should be changed at different temperatures. It is recommended, therefore, that the same type of polymer be applied for the construction of a calibration curve unless the Q -factors obtained in the same solvent at the same temperature are known.

NBS data of polyethylene SRM 1475 were measured on columns of a 20-ft by $3/8$ -in.-diameter polystyrene gel with five 4-ft sections of nominal porosities of 10^3 , 10^4 , 10^5 , 10^6 , and 10^7 Å at 135°C using TCB.⁶ From the weight-average molecular weight of SRM 1475 reported in the literature⁶ and the weight-average extended chain length measured here, the Q -factor for polyethylene was calculated as 17.7, which is consistent with the value in the literature.³

DISCUSSION

As shown in Table II, the Q -factors experimentally obtained for poly-1-olefins from poly-1-hexene to poly-1-octadecene are lower than the theoretical ones, in contrast to those for polyethylene, polypropylene, and poly-1-butene. Polymers in solution are supposed to be contracted rather than being extended; and if the ratios of real size in solution to extended chain length for polyolefins are lower than that for polystyrene, the observed Q -factors for the polymers should be higher than the theoretical ones. Polyethylene and polypropylene fall in this category. Polymers in solution at higher temperature should be more extended than those at lower temperature. Therefore, the extended chain lengths for poly-1-olefins measured at 135°C are easily supposed to be longer than those at 80°C , in contrast to the results shown in Table III as far as the elution count-extended chain length calibration curve for polystyrene is concerned.

In order to explain why poly-1-olefins which have long pendent groups showed different behavior than polyethylene and polypropylene, the assumption has been made that those poly-1-olefins exist in solution as a quasi-rod-shaped polymer (or alternatively as a stiff coil) rather than a random coil. The real size in solution for poly-1-olefin might be longer than that for polystyrene, which has the same extended chain length as the poly-1-olefin due to the effect of the pendent group. Conversely, the influence of the length, which correspond to the radius of the quasi-rod-shaped polymer, of a pendent group for poly-1-olefin on the fractionation cannot be disregarded. A quasi-rod-shaped polymer elutes earlier than a random coil polymer which has the same theoretically calculated extended chain length as the polymer. In consequence, the extended chain length for poly-1-olefin measured is larger than the real extended chain length, and hence the apparent Q -factor becomes smaller than the theoretical one.

It is assumed that poly-1-olefins in solution at 135°C change partially their morphology from a stiff coil to a random one and the effective length for fractionation by GPC such as end-to-end distance becomes smaller. However, the observed extended chain length is still longer than the real

one due to the partial effect of a pendent group, and hence the apparent Q-factors remain at lower values than the theoretical ones.

Two other possibilities should be considered to explain the lower extended chain length observed at 135°C relative to that at 80°C; the thermal degradation of the sample at 135°C and molecular aggregation at 80°C. The possibility of the thermal degradation of poly-1-olefins during their stay in the columns at 135°C was checked by leaving the sample solution at 135°C for 3 hr under nitrogen atmosphere followed by measuring GPC of the solution at 80°C. The average extended chain length of the sample after the heat treatment was somewhat lower relative to that before the heat treatment, but they were still regarded to be identical within the experimental error. Effect of polymer concentration on elution count and molecular weight for polystyrene was reported,⁷ however, the extended chain lengths for poly-1-olefins measured at 80°C were almost unchanged at different polymer concentrations such as one-half or one-quarter of the 0.1% (w/v) which was applied for the major study here. These results do not deny the possibility of molecular aggregation during the chromatographic separation at 80°C, but the corrected Q-factors obtained in this study would be valuable as far as GPC for poly-1-olefins at 80°C is concerned.

This work was done at the Department of Polymer Science and Engineering, University of Massachusetts at Amherst, Massachusetts. The author wishes to express his appreciation to Professor R. S. Porter for advice and encouragement on this work. Special thanks are due to the Department of Polymer Science and Engineering for furnishing the facilities for this research.

References

1. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci.*, **B5**, 753 (1967).
2. K. A. Boni, F. A. Sliemers, and P. B. Stickney, *ibid. A-2*, **6**, 1579 (1968).
3. J. V. Dawkins and J. W. Maddock, *Eur. Polym. J.*, **7**, 1537 (1971).
4. A. C. Ouano and P. L. Mercier, *J. Polym. Sci.*, **C21**, 309 (1968).
5. J. Wang, S. Mori, R. S. Porter, and J. R. Knox, to be published.
6. G. Ross and L. Frolen, *J. Res. Nat. Bur. Stand., Phys. Chem.*, **76A**, 163 (1972).
7. K. A. Boni, F. A. Sliemers, and P. B. Stickney, *J. Polym. Sci. A-2*, **6**, 1567 (1968).

Received December 27, 1973

Revised February 4, 1974