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Molecular Heterogeneity Characterization in Polyglycols

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Synopsis

This paper deals with polydispersity coefficient characterization in poly(propylene glycols) (PPG 425, 750, 1025, 1200, and 2025) and poly(ethylene glycols) (PEG 200, 600, and 1000). The methods used involved ratio of 50% solution to intrinsic viscosity and ratio of weight-average to number-average molecular weight, as determined by gel permeation chromatography, light-scattering photometry, and vapor pressure osmometry. The methods used assigned the same value to this coefficient. Polydispersity in polyglycols, which have low molecular weights ($\leqslant 2200$) and narrow distributions ($\leqslant 1.1$), may thus be determined from viscosity measurements.

INTRODUCTION

An accurate knowledge of polydispersity is important because it influences the physical properties of polymers.[1-4] Depending on whether complete or approximate molecular weight distributions are required, various methods are available for the measurement of this coefficient. For complete molecular weight distributions the usual method is to fractionate the polymer and construct integral and differential molecular weight distribution curves. This method is very time consuming and, moreover, there is not yet available a good analytical method of general application for obtaining narrow fractions.

To obtain approximate molecular weight distributions one has the choice of several short-cut techniques. One such method frequently employed for measuring polydispersity is from the ratio of weight-average to number-average molecular weights, ROM, or $(\overline{M}_w/\overline{M}_n)$ or $(\overline{M}_w/\overline{M}_n) - 1$.[5-7] Reliable information, however, cannot be obtained from this method, if complications in the polymer structure due to microgel[8-11] and branching[12,13] occur. Other measurements that can relate to approximate molecular weight distributions are the ratio of intrinsic viscosity in thermodynamically good and poor solvents,[14] the shear dependence of viscosity,[15,16] the frequency dependence of the real part of a complex viscosity,[17] the stress relaxation,[18] and the relaxation-time distributions.[19] Some of these methods are tedious, and others are unreliable and therefore rarely used.

Recently a simple method[20] was proposed for polydispersity characterization. This method is based on the ratio of concentrated solution viscosity to intrinsic or Mooney viscosity,[21,22] ROV or ROVM. The principle used is that the concentrated solution viscosity is related to a higher moment of molecular weight spread than is either intrinsic or Mooney viscosity. This method is at present in the testing stage and has been applied to SBR structures complicated with microgel.[20] In this work it has been applied to simpler systems such as poly(propylene glycol) (PPG) and poly(ethylene glycol) (PEG), and the results obtained are in agreement with those obtained by standard methods.

Experimental

The PPG and PEG samples were obtained from sources described elsewhere.[23] Concentrated-solution viscosities and intrinsic viscosities were measured at room temperature with methyl ethyl ketone as solvent by means of Brookfield (Model, LVT) and Cannon-Fenske viscometers. Corrections were applied wherever needed. The average molecular weights were determined with a Waters gel permeation chromatograph (GPC), Model, 200, with tetrahydrofuran, and with a Mechrolab vapor pressure osmometer (VPO), Model, 301A and a Brice-Phoenix light-scattering photometer (LS), Model, Universal 2000 series. The vapor pressure osmometry and light-scattering photometry were carried out with methyl ethyl ketone solutions.

Results and Discussion

The variation of viscosity with concentration was studied for three samples and the curves obtained are shown in Figure 1. These curves have three distinct regions, each of which may be represented by

$$\eta = k \exp SC \tag{1}$$

where η is the viscosity, S is the slope, and C is the concentration. It can be seen from these curves that, as one region passes into the other, starting from the first one, the slopes have the following ratios: PEG 200, 1:3:15; PPG 425, 1:2:5; and PPG 2025, 1:2:3.

By a standard curve-fitting method[24] the following equation was found to represent the total curve of PEG 200:

$$\eta = 27.0 \times 10^{-2} \exp \{-7.2 \times 10^{-2}C\} + 33.0 \times 10^{-2} \times \exp \{4.2 \times 10^{-2}C\} + 11.5 \times 10^{-12} \exp \{27.0 \times 10^{-2}C\} \tag{2}$$

Such elaborate curve analysis was not attempted for the other two samples because the results reported are not sufficient to establish any meaningful correlations. The rapid rise in viscosity, however, may be explained in terms of intermolecular interactions.[25–30]

The plots of 50% solution to intrinsic viscosity were linear (Fig. 2*A*), and so the relationship between these two viscosities may be represented by[31]

$$\eta = K'[\eta]^{B/a} \tag{3}$$

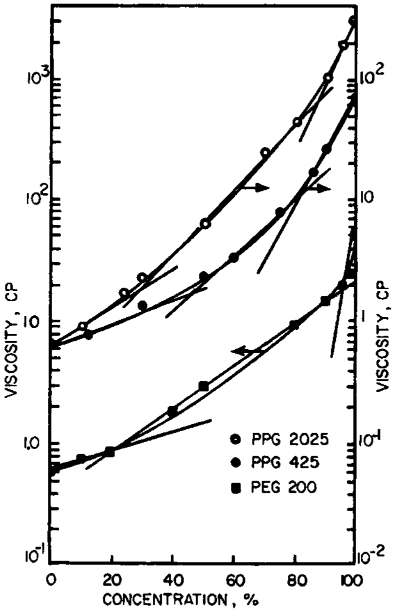

Fig. 1. Variation of viscosity with concentration of polymer.

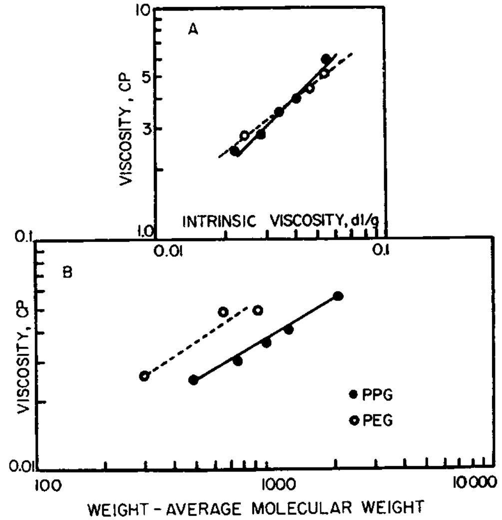

Fig .2. Concentrated-solution (50%) viscosity versus (*A*) intrinsic viscosity and (*B*) weight-average molecular weight.

It is interesting to note here that the linear relation holds in spite of considerable variation in intrinsic viscosities $[\eta]$.

The slope B/a for PPG was found to be 1.0; that for PEG, 0.8. The values of B calculated from the slopes of η versus $\overline{M}_w$ (Fig. 2*B*) according to the equation,[31]

$$\eta = K''(\overline{M}_w)^B \tag{4}$$

were 0.6 (PPG) and 0.7 (PEG). These figures for B are very low compared to the 3.4–7.0 values found for other systems.[32–40]

The exponent a calculated for the two systems studied were 0.6 (PPG) and 0.9 (PEG). The magnitude of these values is in the right range. Both this evidence (e.g., values of a)[41] and the sharp rise in viscosity at high polymer content[42,43] reflect on the thermodynamic suitability of methyl ethyl ketone as a solvent for viscosity measurements of polyglycols.

In Tables I and II the ROV and ROM are given. The ROV obtained from 50% solution to intrinsic viscosity agrees well with the polydispersity, ROM obtained from GPC and LS–VPO. The viscosities of 24% and whole polymer are not suitable for polydispersity characterization, because the former gives unrealistic values and the latter gives molecular weight-dependent values. With high molecular weight materials a low solution viscosity is needed in the characterization of this coefficient.[20]

The samples studied meet all the following conditions necessary for ROV to be operative as a valid heterogeneity index:[20] constant microstruc-

TABLE I
Viscosity Values of Polyglycols

Sample	$[\eta]$, dl./g. ($\times 10^2$)	η, cp. at concn. (%)			ROV at concn. (%)		
		24	50	100	24	50	100
PPG:							
425	2.42	0.85	2.24	65.4	0.4	0.9	27.0
750	2.90	1.00	2.83	107.0	0.4	1.0	37.0
1025	3.50	1.08	3.52	140.8	0.3	1.0	40.2
1200	4.00	1.21	4.14	178.0	0.3	1.0	44.5
2025	5.60	1.60	6.00	326.0	0.3	1.1	58.0
PEG:							
200	2.50	0.96	2.78	50.8	0.4	1.1	20.0
600	4.73	1.19	4.46	136.4	0.3	0.9	28.8
1000	4.97	1.47	5.21	—	0.3	1.0	—

TABLE II
Molecular Weights of Polyglycols

Sample	$\bar{M}_n$		$\bar{M}_w$		ROM	
	VPO	GPC	LS	GPC	LS–VPO	GPC
PPG:						
425	420	370	490	400	1.0	1.1
750	700	690	760	740	1.1	1.1
1025	920	880	1010	980	1.1	1.1
1200	1130	1300	1270	1430	1.1	1.1
2025	1950	2130	2100	2200	1.0	1.0
PEG:						
200	210	270	300	280	1.4	1.1
600	600	530	660	560	1.1	1.1
1000	860	940	940	1010	1.1	1.1

ture and composition, a higher M_w value, and no branching. Another condition, that $[\eta]$ should not vary considerably from sample to sample, is probably not valid in the case of low-viscosity systems.

Polydispersity characterization in polyglycols, which have low molecular weights ($\leqslant 2200$) and narrow distributions ($\leqslant 1.1$), may thus be carried out from the ratio of viscosities $\eta_{50\%}/[\eta]$.

A further test of the ROV parameter will be carried out on other polyglycols[44-47] prepared in this laboratory, on branched structures, and on structures complicated with microgel.

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Résumé

Ce manuscrit discute la caractérisation par le coefficient de polydispersité de polypropylène glycol (PPG 425, 750, 1025, 1200 et 2025) et des polyéthylènes glycols (PEG 200, 600 et 1000). Les méthodes utilisées étaient le rapport des viscosités à 50% à des viscosités intrinsèques et les rapports des poids moléculaires moyens en nombres et poids moléculaires moyens en poids, tels que déterminés par chromatographie par perméation sur gel, photométrie turbidimétrique et osmométrie par pression de vapeur. Les méthodes utilisées attribuaient la même valeur à ce coefficient. La polydispersité dans les polyglycols qui ont de bas poids moléculaires ($\leq$2200) et des distributions étroites ($\leq$1.1), peut donc être déterminé au départ de mesures viscosimétriques.

Zusammenfassung

Die vorliegende Mitteilung befasst sich mit der Charakterisierung von Polypropylenglykolen (PPG 425, 750, 1025, 1200 und 2025) und Polyäthylenglykolen (PEG 200, 600 und 1000) durch den Polydispersitätskoeffizienten. Folgende Methoden wurden verwendet das Verhältnis der Viskosität einer 50%-igen Lösung zur Viskositätszahl und Verhältnis des Gewichtsmittels zum Zahlenmittel des Molekulargewichts, wie es durch Gelpermeationschromatographie, Lichtstreuungsmessung und Dampfdruckosmometric bestimmt wird. Die verwendeten Methoden lieferten den gleichen Wert für den Polydispersitätskoeffizienten. Die Polydispersität von Polyglykolen mit niedrigem Molekulargewicht ($\leq$2200) und enger Verteilung ($\leq$1,1) kann daher durch Viskositätsmessungen bestimmt werden.

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