Viscosity/Molecular-Weight Relationship for γ-(2,3-Dihydroxypropoxy)propyl-Terminated Poly(dimethylsiloxane)s

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ABSTRACT: A series of γ-(2,3-dihydroxypropoxy)propyl-terminated poly(dimethylsiloxane) (DHT-PDMS) samples with different molecular weights were prepared through the acid-catalyzed equilibrium copolymerization of octamethyl-cyclotetrasiloxane and 1,3-bis[γ-(2,3-dihydroxypropoxy)-propyl]tetramethyldisiloxane. The intrinsic viscosity in toluene ($[\eta]_{\text{toluene}}$) and the number-average molecular weight (M_n) were determined with an Ubbelohde viscometer and ^{1}H-NMR spectra, respectively. In this way, the relationship between $[\eta]_{\text{toluene}}$ and M_n was established. For $2.0 \times 10^4 < M_n < 4.0 \times 10^4$, $[\eta]_{\text{toluene,25°C}}$ was $1.874 M_n^{0.323}$. The solution behavior of DHT-PDMS was also investigated. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1759–1762, 2004

Key words: solution properties; viscosity; polysiloxanes

INTRODUCTION

The copolymerization of polysiloxanes and organic polymers can produce organic polymers with the excellent properties of polysiloxanes. The copolymers so obtained exhibit new properties and have great commercial significance and application potential in many fields.[1(a)] Carbofunctionalized polysiloxanes are often used in the copolymerization of polysiloxanes and organic polymers, for which hydroxyalkyl-terminated polysiloxanes play an important role.[1(b)] For example, coatings prepared through the copolymerization of hydroxyethoxylpropylated polysiloxanes and isocyanates have good antifouling properties and resistance to heat, cold, and water.[2] Polysiloxane-*co*-polyurethanes from hydroxypropyl-terminated polysiloxanes and 4,4'-diphenylmethane diisocyanate show excellent biocompatibility.[3] Kanno and coworkers[4,5] found that polyesters modified with hydroxybutyl-terminated polysiloxanes exhibited not only high strength but also good flexibility and resistance to impact, heat, hydrolysis, and chemicals. Polysiloxane-*co*-polycarbonates from phenolic hydroxyl-terminated polysiloxanes and bisphenol A show high oxygen and water permeability, film-forming ability, and good mechanical properties and processability.[6−9] In previous research, monohydroxyalkyl-terminated polysiloxanes have mainly been involved. However, dihydroxyalkyl-terminated polysiloxanes, such as γ-(2,3-dihydroxypropoxy)propyl-terminated poly(dimethylsiloxane) (DHT-PDMS),
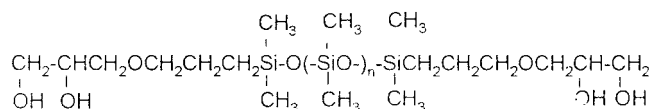
may be preferable for the modification of organic polymers to monohydroxyalkyl-terminated ones because of the reaction activity of the dihydroxyl groups, and they will probably be used more widely after modification research.

The first concern for the use of hydroxyalkyl-terminated polysiloxanes is their molecular weight. The determination of the number-average molecular weight (M_n) of a polymer by its intrinsic viscosity ($[\eta]$) is convenient, economical, and prompt after the relationship between $[\eta]$ and M_n has been determined. Furthermore, $[\eta]$ of a polymer also indicates its solution behavior. The relationship between $[\eta]$ of poly(dimethylsiloxane)s,[10−13] aminopropyl-terminated polysiloxanes,[14] epoxy-terminated polysiloxanes,[15] and hydroxypropyl-terminated polysiloxanes[16] and M_n has been well investigated. In this way, a very convenient way of determining M_n for those polysiloxanes has been provided. To the best of our knowledge, the relationship between $[\eta]$ and M_n of DHT-PDMS has not been previously reported. In this work,

TABLE I
Experimental Results for the Preparation of DHT-PDMS

Sample	D_4 (g)	DH (g)	A-clay (g)	TFMSA (μL)	Yield (%)
1	20.00	0.50		6.0	70.0
2	22.50	0.60		6.0	77.6
3	28.65	1.57	1.50		82.8
4	24.60	0.92	1.50		85.6
5	25.50	0.70	1.50		90.5
6	25.00	0.35		4.0	80.0
7	26.55	0.49	1.50		90.2
8	25.25	0.39	1.50		90.3
9	25.00	0.30		4.0	75.2

the relationship between $[\eta]$ and M_n of DHT-PDMS is discussed. The solution behavior of DHT-PDMS in toluene is also analyzed.

EXPERIMENTAL

Apparatus and reagents

^{1}H-NMR spectra were recorded on a Bruker ARX 300-MHz instrument (Rheinstetten, Germany). Ubbelohde viscometers were acquired from the Glass Apparatus Firm of Shandong University (Jinan, China). Toluene was dried over sodium and distilled before use. Octamethylcyclotetrasiloxane (D_4), trifluoromethanesulfoonic acid (TFMSA), and activated clay (A-clay), all chemical reagents, were used without further purification. 1,3-Bis[γ-(2,3-dihydroxypropoxy)propyl]tetramethyldisiloxane (DH) was prepared in our laboratory.

Preparation of DHT-PDMS

According to a method used in our previous work,[17] a series of DHT-PDMS samples with different molecular weights were prepared through the copolymerization of D_4 and DH with A-clay or TFMSA as a catalyst. The results are summarized in Table I.

Determination of M_n

The structures of DHT-PDMS were analyzed by ^{1}H-NMR spectra. M_n's of DHT-PDMS were determined from proton integral ratios of two kinds of different groups and were calculated as follows:

$$M_n = \frac{\left(\frac{1}{3}a/2\right) - 2}{\frac{1}{7}b/2} \times 74 + 398$$

where a is the proton integral value of Si—CH_3 groups ($\delta = 0.1$ ppm), b is the proton integral value of

—$CH_2CHCH_2OCH_2$— groups ($\delta = 3.0$–3.7 ppm), 74 is the molecular weight of the $(CH_3)_2SiO$ unit, and 398 is the molecular weight of DH. The results are collected in Table II.

Measurement of $[\eta]$

The viscosities of DHT-PDMS solutions of different concentrations in toluene were measured at $25 \pm 0.1°C$ with an Ubbelohde viscometer. $[\eta]$ was determined by the extrapolation of the specific viscosity (divided by the concentration) to the corresponding zero concentration with the method of averages.[14] The results are listed in Table II. Kinetic corrections were not applied to the viscosity measurements.

RESULTS AND DISCUSSION

The experiments showed that the periodate oxygenation method[18] with water as a solvent and the esterification method[19] with phthalic anhydride and pyridine as a solvent could not successfully determine the end hydroxyl values of DHT-PDMS to obtain their M_n's. Therefore, we chose the ^{1}H-NMR method, which has been proved to be accurate and effective.

In DHT-PDMS, adjacent dihydroxyl groups are added to the ends of linear poly(dimethylsiloxane)s. Because the properties of adjacent dihydroxyl groups decide the behavior of DHT-PDMS in solution to a great extent, which is especially different from that of methyl-terminated poly(dimethylsiloxane) (PDMS), α,ω-dihydroxypoly(dimethylsiloxane) (HO-PDMS), γ-(2,3-epoxypropoxy)propyl-terminated poly(dimethylsiloxane) (EP-PDMS), aminopropyl-terminated poly-(dimethylsiloxane) (NH-PDMS), and hydroxypropyl-terminated poly(dimethylsiloxane) (HOP-PDMS) with respect to the relationship between $[\eta]$ and M_n, it is necessary and important to investigate the relationship between the intrinsic viscosity in toluene ($[\eta]_{\text{toluene}}$) of DHT-PDMS and M_n and the solution behavior of DHT-PDMS.

DHT-PDMS is a kind of linear polymer with flexible molecular chains and can be dissolved in toluene.

TABLE II
M_n and $[\eta]$ of DHT-PDMS

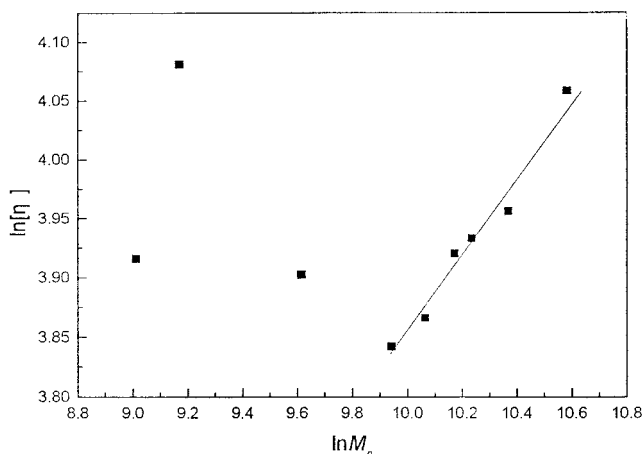| Sample	$M_n \times 10^3$	$[\eta]_{\text{toluene, 25°C}}$
1	8.2	50.21
2	9.6	59.21
3	15.0	49.51
4	20.8	46.60
5	23.5	47.75
6	26.2	50.42
7	27.9	51.04
8	31.9	52.23
9	39.5	57.86

Figure 1 ln [η] versus ln M_n.

Therefore, the relationship between [η]$_{\text{toluene}}$ and M_n of DHT-PDMS should agree with the Mark–Houwink equation:[20]

$$[\eta] = kM_n^a \tag{1}$$

Equation (1) can be changed into a natural logarithm:

$$\ln [\eta] = \ln k + \alpha \ln M_n \tag{2}$$

where k and α are constants, which can be obtained from the intercept and slope, respectively, of ln [η] $\sim$ ln M_n (a straight line).

According to the experimental results in Table II, a straight line of ln [η] versus ln M_n (Fig. 1) was plotted, and from it k (1.874) and α (0.323) for $2.0 \times 10^4 < M_n < 4.0 \times 10^4$ were obtained. Therefore, the relationship between [η] and M_n of DHT-PDMS can be given as follows for $2.0 \times 10^4 < M_n < 4.0 \times 10^4$:

$$[\eta]_{\text{toluene,25°C}} = 1.874M_n^{0.323} \tag{3}$$

When M_n is less 2.0×10^4, the relationship between [η] and M_n deviates from eq. (3).

Parameters k and α are related to the structures of the macromolecular chains and the morphologies of the macromolecular balls in given solvents and at given temperatures. Most of the polymers are in the form of high spread balls in solutions. Solvents are associated with the balls because of solvation. The experiments have demonstrated that for polymers with morphologies of atactic macromolecular balls, their α values in solvents are between 0.5 and 1.0 at a given temperature. Most are between 0.6 and 0.8. In this case, the solvents are good for the polymers, and macromolecular chains are unfolded. In poor or poorer solvents, the α values of the polymers are small because the macromolecular balls are tightened. The data in Table II show that when the molecular weight

of DHT-PDMS is low and its hydroxyl value is high, [η]$_{\text{toluene}}$ is particularly large. For example, the [η] values of DHT-PDMS with molecular weights of 8200, 9600, and 15,000 are 50.21, 59.21, and 49.51, respectively, being even larger than those of DHT-PDMS with molecular weights of 20,800 and 23,500. This allows us to assume that high hydroxyl values of DHT-PDMS cause the large effects of the hydrogen bonds and molecular polarity on the morphology of the DHT-PDMS molecules in solution, so that the DHT-PDMS molecules are slightly folded in toluene and deviate the morphology of the atactic balls, leading to an increase in [η]. This, of course, should be attributed to a joint effect of the hydroxyl groups and molecular weight of DHT-PDMS. When the molecular weights of DHT-PDMS are low, the effects are especially obvious because of the high hydroxyl values. The α value of 0.323 suggests that toluene is not a very good solvent for DHT-PDMS because of the polarity of the adjacent double hydroxyl groups. This also shows that although the amounts of the adjacent double hydroxyl groups in DHT-PDMS are not too large, they can alter the properties of the polysiloxanes. Only when the molecular weights of DHT-PDMS are large enough does the relationship between [η]$_{\text{toluene}}$ and M_n agree with the Mark–Houwink two-parameter equation.

The Mark–Houwink equations of some polysiloxanes are as follows. For PDMS[11] and $1.06 \times 10^4 \leq M_n \leq 9.70 \times 10^4$,

$$[\eta]_{\text{toluene, 25°C}} = 8.28 \times 10^{-3}M_n^{0.72} \tag{4}$$

For NH-PDMS[14] and $4.00 \times 10^4 \leq M_n \leq 6.00 \times 10^4$,

$$[\eta]_{\text{toluene,25°C}} = 5.26 \times 10^{-2}M_n^{0.587} \tag{5}$$

For EP-PDMS[15] and $2.50 \times 10^3 \leq M_n \leq 2.50 \times 10^4$,

$$[\eta]_{\text{toluene,25°C}} = 6.0 \times 10^{-4}M_n^{0.60} \tag{6}$$

For HO-PDMS[10] and $2.50 \times 10^3 \leq M_n \leq 2.00 \times 10^5$,

$$[\eta]_{\text{toluene,25°C}} = 2.0 \times 10^{-4}M_n^{0.66} \tag{7}$$

For HOP-PDMS[16] and $1.38 \times 10^4 < M_n < 2.88 \times 10^4$,

$$[\eta]_{\text{toluene,25°C}} = 0.3183M_n^{0.510} \tag{8}$$

If we compare eq. (3) with eqs. (4)–(8), we can found that the relationship between [η] and M_n of DHT-PDMS is quite different from that of PDMS, HO-PDMS, EP-PDMS, HOP-PDMS, and NH-PDMS. For the end groups of those polysiloxanes, α is in the

following order: $-CH_2CH_2CH_2OCH_2CH(OH)CH_2OH$ < $-CH_2CH_2CH_2OH$ < $-CH_2CH_2CH_2NH_2$ < $-CH_2$-$CH_2CH_2OCH_2\,CH\text{-}CH_2$

$$\underset{O}{\overset{\diagup\diagdown}{}}$$

< $-OH$ < CH_3. In other words, the solubility of polysiloxanes with different end groups in toluene decreases in the following order: DHT-PDMS < HOP-PDMS < NH-PDMS < EP-PDMS < HO-PDMS < PDMS. This suggests that the end groups and their polarity are the deciding factors in determining the relationship between $[\eta]$ and M_n of polysiloxanes. The stronger the polarity is of the end groups, the smaller α is. In the aforementioned polysiloxanes, DHT-PDMS has the smallest α value, 0.323, because the double hydroxyl end groups have the strongest polarity.

CONCLUSIONS

DHT-PDMS samples of various molecular weights were prepared through the copolymerization of D_4 and DH by acid-catalyzed equilibration with A-clay or trifluoromethanesulfonic acid as a catalyst. $[\eta]_{toluene}$ and M_n were determined with an Ubbelohde viscometer and ^1H-NMR spectra, respectively. For $2.0 \times 10^4 < M_n < 4.0 \times 10^4$, the relationship between $[\eta]$ and M_n of DHT-PDMS agreed with $[\eta]_{toluene,25°C} = 1.874M_n^{0.323}$. When M_n was less than 2.0×10^4, this relationship was not true because the DHT-PDMS molecules were folded in toluene solutions.

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