# Viscosity–Molecular Weight Relationship for Aminopropyl-Terminated Poly(dimethylsiloxane)

**YONGZHONG WU, SHENGYU FENG**

Institute of New Materials, Shandong University, Jinan, Shandong 250100, People's Republic of China

**ABSTRACT:** Aminopropyl-terminated poly(dimethylsiloxane) (ATPS) with different molecular weights was prepared by base-catalyzed equilibration of octamethylcyclotetrasiloxane and 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with different ratios. Their number-average molecular weights ($M_n$) were determined by end–group analysis, and intrinsic viscosity ($[\eta]$) in toluene was measured with a Ubbelohde viscometer. A relationship between $M_n$ and $[\eta]$ was obtained for ATPS. For $1.0 \times 10^4 < M_n < 6.0 \times 10^4$, it was in accord with $[\eta]_{\text{toluene,25°C}} = 5.26 \times 10^{-2} M_n^{0.587}$. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 975–978, 2001

**Key words:** viscosity; molecular weight; relationship; aminopropyl groups; poly(dimethylsiloxane)

## INTRODUCTION

Polysiloxane exhibits unique properties such as low glass-transition temperature ($T_g$), good UV and thermal stability, biocompatibility, low surface energy, and high oxygen permeability.[1] An effective means of modifying organic polymers with the unique properties of polysiloxane is to combine polysiloxane with organic polymers through chemical bonds or in other ways. Functionally reactive polysiloxane can react with many kinds of polymers and produce grafted or segmented copolymers. Functionally reactive polysiloxane and its copolymers with organic polymers have been widely studied during the last decades, and they have been found to be of great commercial significance.[2]

Aminopropyl-terminated poly(dimethylsiloxane) (ATPS) is an important precursor for the synthesis of a variety of multiphase copolymers because of the reactivity of its aminopropyl groups.[3] For example, when ATPS is combined with polyimide, the processing temperature and hydroscopicity of the polyimide are decreased,[4,5] and when combined with polyamide, the impact resilience and frictional characteristics of the polyamide are improved, and the copolymers can be made into selectively permeable membranes.[6,7] When combined with polyurethane, the latter can be used as thermoplastic elastomers and medical materials.[8,9] Because of these extensive uses and the especially promising applications of ATPS, more attention is being paid to it. Although studies on the preparation and copolymerization of ATPS have already been reported, no attempt had ever been made to study the basic characteristics of ATPS. The number-average molecular weight ($M_n$) of ATPS is an important structural parameter. Can the $M_n$ be determined easily? Generally speaking, after the relationship between intrinsic viscosity $[\eta]$ of a solution of some polymer with its $M_n$ has been determined, the determination of its $M_n$ by $[\eta]$ will be an important and convenient method. In order to solve the problem mentioned above, we synthesized a series of ATPS with different molecular

**Table I**  $M_n$ and $[\eta]$ of ATPS

|  | ATPS-1 | ATPS-2 | ATPS-3 | ATPS-4 | ATPS-5 | ATPS-6 | ATPS-7 |
|---|---|---|---|---|---|---|---|
| $N \times 10^3$ (mol/g) | 19.20 | 11.72 | 10.87 | 6.93 | 5.70 | 3.69 | 3.35 |
| $Mn$ (g/mol) | 10418 | 17067 | 18397 | 28840 | 35096 | 54178 | 59650 |
| $[\eta]_{\text{toluene,25°C}}$ (mL/g) | 11.92 | 16.83 | 17.46 | 22.39 | 24.95 | 29.51 | 33.88 |

weights, measured their $M_n$ by end-group analysis, and their $[\eta]$ in toluene at 25°C with a Ubbelohde viscometer, and thus obtained the relationship between $M_n$ and $[\eta]$ of ATPS.

## EXPERIMENTAL

### Apparatus and Regents

A Ubbelohde viscometer was generously supplied by the glass apparatus firm of Shandong University. A standard solution of perchloric acid–glacial acetic acid (0.01 mol:l $HClO_4$—$CH_3COOH$) was prepared according to the method outlined by Sun.[10] Glacial acetic acid, toluene, and chloroform were obtained from the chemical reagent firm of Jinan, Shandong, People's Republic of China.
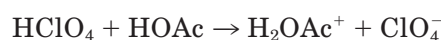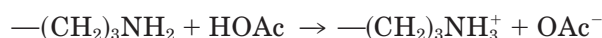
### Samples

According to the method detailed by Geure et al.,[11] we synthesized ATPS samples by the tetramethylammonium siloxanolate[12] catalyzed bulk equilibrium reaction of octamethylcyclotetrasiloxane ($D_4$) with a 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (AT) end blocker. The equilibrium was maintained at 80°C for 24 h, and then the reaction temperature was increased to 150°C to decompose the catalyst. The polymers were vacuum-distilled (at 150°C) to remove the equilibrium cycles. By changing the ratios of $D_4$ to AT, seven ATPS samples were obtained (Table I).

### Determination of Number-Average Molecular Weights

From the characterization of anionic polymerization, we knew these samples have a narrow distribution of molecular weights,[13] also attested to by the GPC spectrum (Fig. 1). It can be seen from the spectrum that the $M_w/M_n$ is 1.31, so ATPS has a very narrow molecular-weight distribution.

End analysis of ATPS in a nonaqueous system determined its amount of amine (N), from the $M_n$

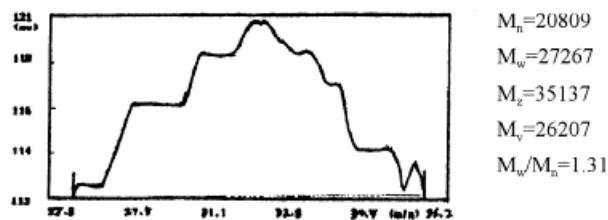could be deduced. The mechanism of titration in a nonaqueous system is illustrated here.

$$—(CH_2)_3NH_2 + HOAc \; \rightarrow \; —(CH_2)_3NH_3^+ + OAc^-$$

$$HClO_4 + HOAc \rightarrow H_2OAc^+ + ClO_4^-$$

$$H_2OAc^+ + OAc^- \rightarrow 2 \; HOAc$$

Glacial acetic acid plays the role of transporting protons among amines and perchloric acid molecules.
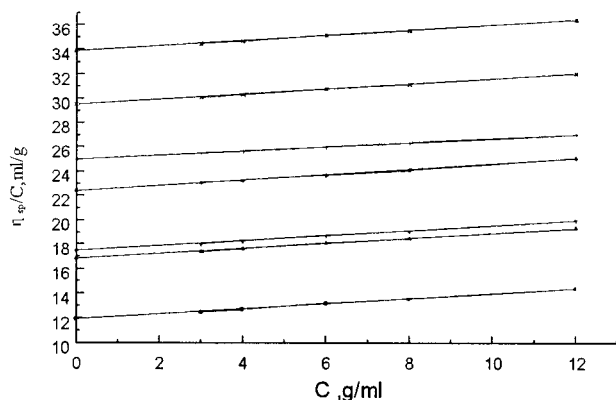
After weighing the sample containing exactly $0.06 \approx 0.09$ mmol amine, we put it in a 50-mL beaker equipped with a magnetic stirring bar. Then 20 mL of chloroform, 10 mL of glacial acetic acid, and 0.1 mL crystal-violet glacial acetic acid solution[10] were charged to the beaker. While stirring at room temperature, the mixture was titrated with 0.01 mol/l of a perchloric acid–glacial acetic acid standard solution. When the color of the solution abruptly changed from violet to blue, the test was ended. Another titration test without samples, that is, with blank titration, was done by the same method. The amount of amino groups and the $M_n$ of ATPS were calculated according to the following two equations:

$$N = C * (V - V_0)/1000 * W \qquad (1)$$

$$Mn = 2/N \qquad (2)$$



| | M$_n$=20809 |
|---|---|
| | M$_w$=27267 |
| | M$_z$=35137 |
| | M$_v$=26207 |
| | M$_w$/M$_n$=1.31 |

**Figure 1**  GPC spectrum of ATPS.

**Figure 2** $[\eta]_{sp}/c$ versus $c$ for ATPS in toluene at 25°C.

where $N$ is the amount (mol/g) of amino groups in ATPS, $M_n$ is the number-average molecular weight (g/mol) of ATPS, $C$ is the concentration (mol/l) of perchloric acid–glacial acetic acid solution, $V$ is the volume (mL) used in the sample tests, $V_0$ is the volume (mL) used in the blank test, and $W$ is the weight (g) of the samples. The results obtained are shown in Table I.

**Determination of Intrinsic Viscosity**

The viscosities of seven ATPS samples in toluene at 25 ± 0.1°C were measured with a Ubbelohde viscometer. The results obtained are shown in Figure 2. The intrinsic viscosities, $[\eta]$, shown in Table I, were determined by the extrapolation of $\eta_{sp}/c$ to a zero concentration by using the method of averages. Kinetic corrections were not applied to the viscosity measurements.

## RESULTS AND DISCUSSION

Aminopropyl-terminated poly(dimethylsiloxane) is a flexible linear polymer. In a good solvent (such as toluene) and at certain temperatures, the $M_n$ and $[\eta]$ of ATPS should be in accord with the Mark–Houwink empirical equation[14]:

$$[\eta] = K * M^a \qquad (3)$$

The logarithm of eq. (3)—to the base $n$, 2.71828— produces linear eq. (4):

$$\ln[\eta] = \ln K + a \ln M \qquad (4)$$

After taking the logarithms of the $[\eta]$ and $M_n$ obtained from the experiments, they were linear-

ized using BASIC, producing the coefficients $K$ (= 0.0526) and $\alpha$ (= 0.587) of the returning equation and the related coefficient $R$ (= 0.99898).

Using another method produced the plot of ln $[\eta]$ versus ln $M_n$ (Fig. 3). The intercept and the slope of the plot can be seen from Figure 3: ln $K$ =2.9188, or $K$ = 0.054 and $\alpha$ = 0.587.

The values obtained from the two methods mentioned above are consistent. So the relationship of $[\eta]$ to $M_n$ of ATPS for $1.0 \times 10^4 < M_n < 6.0 \times 10^4$ is:

$$[\eta]_{\text{toluene,25°C}} = 5.26 \times 10^{-2} Mn^{0.587} \qquad (5)$$

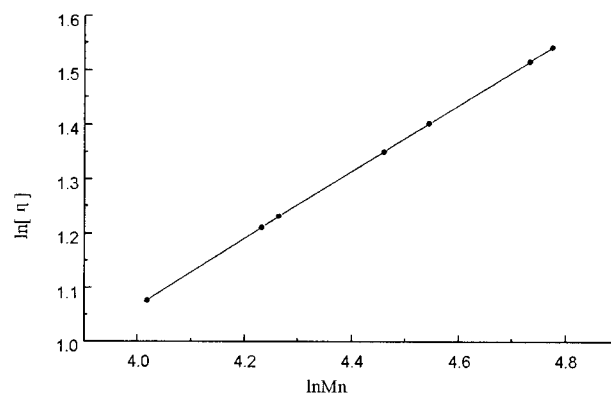For methyl-determined poly(dimethylsiloxane), the relationship of $[\eta]$ to $M_n$ for $2.09 \times 10^5 < M_n < 4.82 \times 10^5$ is[15]:

$$[\eta]_{\text{toluene,25°C}} = 1.17 \times 10^{-2} Mn^{0.71} \qquad (6)$$

For hydroxyl-terminated poly(dimethylsiloxane), the relationship between $[\eta]$ and $M_n$ for $2500 < M_n < 2 \times 10^5$ is[16]:

$$[\eta]_{\text{toluene,25°C}} = 2 \times 10^{-4} Mn^{0.66} \qquad (7)$$

Comparing eq. (5) with eqs. (6) and (7), a difference among them can be seen, that is, when the end groups of poly(dimethylsiloxane) are —$CH_3$, —OH, and —$CH_2CH_2CH_2NH_2$, the coefficient $\alpha$ is in the order of $CH_2CH_2CH_2NH_2 <$ OH $<$ $CH_3$. This difference may be explained by the different end groups. In fact, the values of coefficients $K$ and $\alpha$ depend on the polymer chain structures, the forms of line mass in special solvent, and temperature. Because of the strong polarity of the aminopropyl groups, aminopropyl-terminated poly(dimethylsiloxane) molecules attract each



**Figure 3** ln $[\eta]$ versus ln $M_n$.

other, making it difficult for them to move in toluene and resulting in a big coefficient $K$. In other words, aminopropyl-terminated poly(dimethylsiloxane) has larger $[\eta]$ values compared to methyl- and hydroxyl-terminated poly(dimethylsiloxane) with the same molecular weight.

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