

Ion Aggregation in the Polysiloxane Ionomers Bearing Pendant Quaternary Ammonium Groups

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ABSTRACT: Polysiloxane ionomers bearing pendant quaternary ammonium groups were synthesized through the Menshutkin reaction of poly(γ -chloropropylmethylsiloxane-co-dimethylsiloxane) with *N,N*-dimethylbenzylamine. Ion aggregation in the ionomers with different contents of the quaternary ammonium groups was investigated by torsion braid analysis, transmission electron microscopy, and rheological measurements. It was found that the incorporation of the quaternary ammonium groups did not make a significant effect on the glass transition temperature of the polysiloxane matrix. The glass transition of the cluster phase was found in the range of -20 – 40°C , depending on the concentration of the ion pair. The cluster phase was visualized under TEM when the concentration of the quaternary ammonium group exceeded a critical value. It was indicated by rheological data that the movement of polymer chains in the cluster phase of the polysiloxane ionomers was not restricted at the room temperature, which might be related to the weaker interaction between the bulky quaternary ammonium ion pairs. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 3099–3104, 2002; DOI 10.1002/app.10009

Key words: polysiloxane ionomer; quaternary ammonium group; ion aggregation; dynamic mechanical property; rheological behavior

INTRODUCTION

The ionic polymer represents a broad class of polymers with ionic groups attached to the polymer chain. The ionic polymers having a content of ionic unit below 15 mol % are usually referred to as ionomers.^{1–3} It is usually the case that incorporation of a small amount of ionic group gives rise to great changes in the properties of the parent polymer. During the past three decades, a great deal of research on ionomers has been carried out. Now, ionomers are very important in the area of engineering plastics, thermoplastic elastomers, packing materials, adhesives, and other functional materials.

Properties of an ionomer depend on both the ion pairs and the passive backbone. Polydimethylsiloxanes have a —Si—O—Si— main chain and closely packed pendant methyl groups. They have unique properties such as biological inertness, very low surface energy, heat resistance, and low-temperature flexibility. Therefore, it is of great interest to introduce ionic units to the polysiloxane. Polysiloxane ionomers with sulfonate groups,⁴ carboxylate groups,⁵ and quaternary ammonium salt groups^{6,7} have been declared in patents.

In this article, we report on the preparation and aggregation of polysiloxane ionomers bearing pendant groups with quaternary ammonium chloride moiety. The quaternary ammonium chloride units improve the compatibility of the polysiloxane with organic polymers and bring antimicrobial and antielectrostatic properties to the mate-

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Table I The Chain Composition of the Polysiloxane Ionomers

Sample Code	Chain Composition (mol %)			
	(CH ₃) ₃ SiO—	—(CH ₃) ₂ SiO—	CPMS ^a	BDMAPMS ^b
BDMA-0	3.2	86.8	10.0	0
BDMA-1	3.2	86.8	8.7	1.3
BDMA-2	3.2	86.8	7.7	2.3
BDMA-4	3.2	86.8	5.9	4.1
BDMA-7	3.2	86.8	3.3	6.7
BDMA-10	3.2	86.8	0	10.0

^a γ -chloropropylmethylsiloxy unit.

^b γ -(benzyltrimethylamino)propylmethylsiloxy unit.

rials to make them applicable for fabric-conditioning agents, bacteriocides, textile finishing, and plastic processing.

EXPERIMENTAL

Materials

Poly(γ -chloropropylmethylsiloxane-*co*-dimethylsiloxane) with trimethylsiloxy terminal groups was synthesized in this laboratory. It had a number-average molecular weight M_n of 5000 (determined by VPO method) and a content of the γ -chloropropylmethylsiloxy unit 10 mol % (Cl 4.42 wt %, determined by elemental analysis). *N,N*-dimethylbenzylamine and *n*-butanol were analytic reagents from Beijing Chemicals Factory.

Preparation of Polysiloxane Ionomers

The Menshutkin reaction was carried out for the preparation of the polysiloxane ionomers. For example, in a 500-mL three-necked flask, poly(γ -chloropropylmethylsiloxane-*co*-dimethylsiloxane) 140.0 g, *N,N*-dimethylbenzylamine 71.2 g, and *n*-butanol 106 g were charged; the reactants were heated for 60 h at 103°C under nitrogen atmosphere. The solvent *n*-butanol and the excess tertiary amine were removed by rotary evaporation in vacuum. It was found by ¹H-NMR spectra that all γ -chloropropylmethylsiloxy (CPMS) units were converted into γ -(benzyltrimethylamino)propylmethylsiloxy (BDMAPMS) units. By changing the reaction time, the polysiloxanes with different contents of the quaternary ammonium unit were prepared. The chain compositions of the ionomers prepared for this study are given in Table I.

Torsion Braid Analysis

Torsion braid analysis (TBA) was carried out according to the method of Gillham.⁸ The pendulum was attached to a glass fiber braid coated with the sample. The period of the oscillation (P) and the amplitude of the oscillation (A_n) of the torsion pendulum were measured and recorded by a computer. The relative rigidity and the logarithmic decrement were calculated according to the formulas:

$$\text{Relative rigidity} = \frac{1}{P^2}$$

$$\text{Logarithmic decrement} = \ln \frac{A_n}{A_{n+1}}$$

For TBA analysis, the specimens were prepared by dipping a glass fiber braid in a 20 wt % polysiloxane ionomer solution in acetone (except the sample BDMA-0 in bulk). They were dried in a vacuum oven at 50°C for 5 h. The measurements were conducted with a heating rate of 2°C/min.

TEM Study of the Ionomers

The agglomeration in the polysiloxane ionomers was observed under a Hitachi H800 transmission electronic microscope. For TEM studies, a drop of 1 wt % polymer solutions in *n*-butanol was dried on a carbon-coated mica sheet to form a film; it was then transferred to a copper grid and dried in a vacuum oven at 50°C for 24 h. The specimens were stained in ruthenium tetroxide vapor for 5 h to improve the image contrast.

Rheological Measurement

Steady shear measurements were carried out by using a DSR 200 rheometer (Rheometric Co.) with

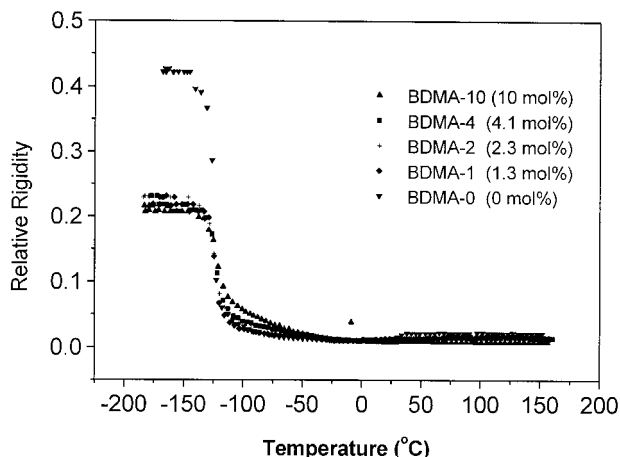


Figure 1 Relative rigidity versus temperature for the polysiloxane ionomers bearing different contents of benzyl dimethyl- γ -silylpropyl ammonium chloride pendant groups. The ion group content is shown in the figures. The formula for calculation of the relative rigidity is given in the experimental part.

a parallel plate geometry with a radius of 25 mm and a gap of 0.5 mm. The temperature dependence of viscosity was measured by using a VEB Rheotest 2 with a cone-and-plate geometry. The upper cone had a radius of 24 mm and an angle of 0.3° . Measurements were conducted in the range of 10 – 85°C at a constant shear rate of 5.56 s^{-1} . The temperature was regulated through a liquid circulation thermostat.

RESULTS AND DISCUSSION

Transitions in the Polysiloxane Ionomers

The polysiloxane ionomers have a very flexible polymer chain, with the pendant quaternary ammonium chloride distributed randomly along the chain. It is generally accepted that the pendant ion pairs associate together to form multiplets. As the ion concentration exceeds a critical value, multiplets aggregate into ion-rich domains, which are referred to as clusters. It is convenient to use the TBA technique for studying the aggregation in the polysiloxane ionomers. The spectra of the relative rigidity and the mechanical damping versus temperature reflect the changes in the mobility of the chain segments in different phases.⁸

Figure 1 shows the curves of the relative rigidity versus temperature for the polysiloxane ionomers. There is a drop of the relative rigidity at ca.

-120°C for all the samples. This is certainly due to the glass transition in the matrix phase.

Two-phase structure of the ionomers can be demonstrated by the dual glass transition, indicated by the damping peaks in the dynamic mechanical spectra. In Figure 2, the curves of logarithmic decrement versus temperature for the polysiloxane ionomers are shown.

The damping peaks located at ca. -120°C , designated T_{g1} , were attributed to the glass transition in the matrix region. The fact that T_{g1} for the ionomers positioned close to the glass transition temperature (-123°C) of polydimethylsiloxane⁹ indicated a very complete phase separation in these ionomers.

The damping peaks at the higher temperature, designated T_{g2} , were attributed to the glass transition in the cluster phase. It is seen that the parent poly(γ -chloropropylmethylsiloxane-*co*-dimethylsiloxane) was phase-separated too, with a glass transition temperature of -75°C . The data of transition temperatures for the ionomers are given in Table II.

It is clear that incorporation of the quaternary ammonium groups enhanced the intermolecular interaction in the ion-rich domains and thus made T_{g2} of the polysiloxane ionomers much higher than that of the parent poly(γ -chloropropylmethylsiloxane-*co*-dimethylsiloxane). In this transition, the ion-ion attraction was overwhelmed by the thermal energy, and the segment movement became free.

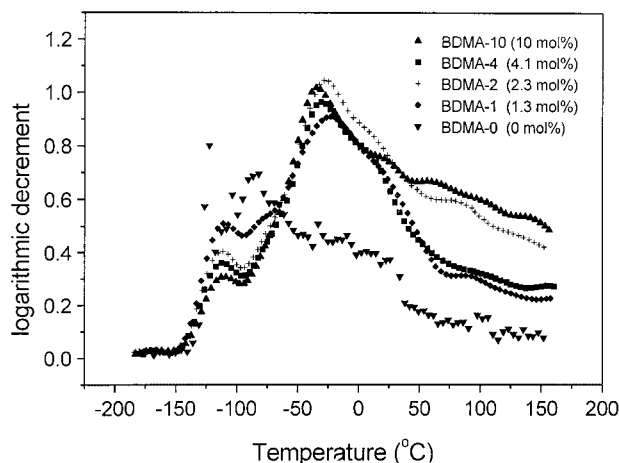


Figure 2 Logarithmic decrement versus temperature for the polysiloxane ionomers bearing different contents of benzyl dimethyl- γ -silylpropyl ammonium chloride pendant groups. The ion group content is shown in brackets in the figures. The formula for calculation of the logarithmic decrement is given in the experimental part.

Table II Transition Temperatures for Polysiloxane Ionomers

Sample Code	BDMAPMS Content (mol %)	T_{g1} (°C)	T_{g2} (°C)
BDMA-0	0	-119	-75
BDMA-1	1.3	-120	-27
BDMA-2	2.3	-120	-21
BDMA-4	4.1	-122	-35
BDMA-10	10.0	-121	-38

It should be pointed out that the changes in the relative rigidity at T_{g2} were not significant. These results are understandable considering that the T_{g2} transition was in the dispersed phase.

TEM Observation of the Ion Aggregation

To visualize the cluster phase in the polysiloxane ionomer, we used the TEM technique. It was found that the image contrast could be improved by staining in ruthenium tetroxide vapor.

In Figure 3, TEM micrographs for the polysiloxane ionomers with different contents of the quaternary ammonium group are shown. Spherical domains are seen in the ionomer samples with a BDMAPMS unit content of 2.3 mol % and higher. The size of the cluster phase increased with the concentration of the ionic unit. The approximate average diameters of 15, 22, and 30 nm

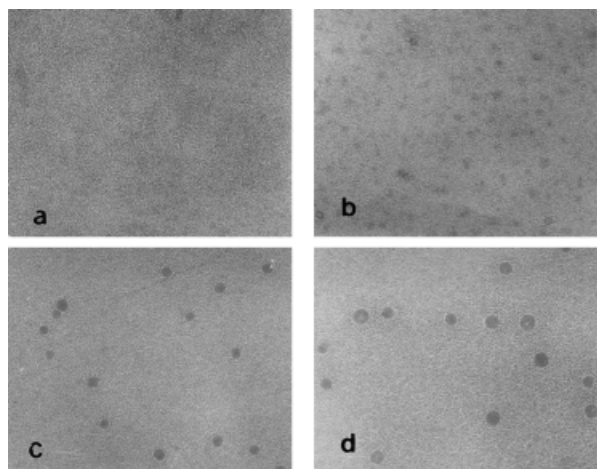


Figure 3 TEM micrographs (magnification 5×10^4) for the polysiloxane ionomers with different contents of the BDMAPMS unit: (a) 1.3 mol %, (b) 2.3 mol %, (c) 4.1 mol %, and (d) 10.0 mol %.

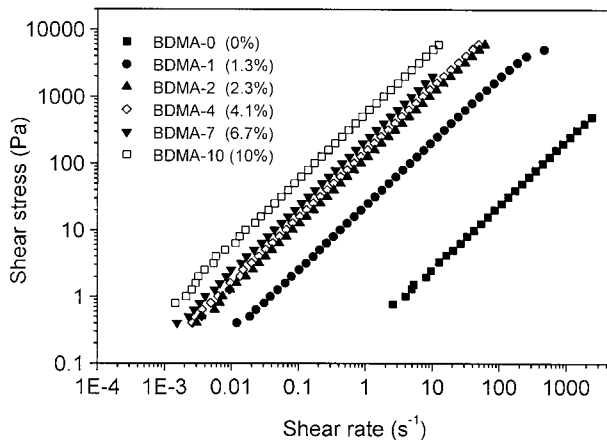


Figure 4 Shear stress versus shear rate at 20°C for the siloxane ionomers. The molar percentage of the quaternary ammonium chloride is shown.

were estimated for the ionomers of BDMA-2, BDMA-4, and BDMA-10, respectively.

In the ionomer BDMA-1, no discrete domains could be seen in the TEM micrograph, although a glass transition of the cluster phase was indicated by the damping peak (Fig. 2) for the ionomer. It is likely that the critical ion concentration (CIC) changed with temperature: as the temperature increased from ca. -20°C to ca. $+20^\circ\text{C}$, the cluster phase in the ionomer BDMA-1 dissolved. The CIC at room temperature should be above 1.3 mol % for the polysiloxane ionomers with the pendant quaternary ammonium chloride.

Rheological Behavior of the Polysiloxane Ionomers

Although the glass transition is relevant to the segment movement, the flow is related to the movement of a whole polymer chain. We measured the flow behavior of the polysiloxane ionomers at a temperature $\sim 40^\circ\text{C}$ above the glass transition temperature of the cluster phase to illustrate the chain movement in these materials.

The rheological behavior of the polysiloxane ionomers in simple shear is shown in Figures 4 and 5. It is seen that the shear stress changed linearly with the shear rate, and the apparent viscosity was almost independent of the shear rate. In a word, the polysiloxane ionomers behaved as Newtonian fluid in the range of shear rate for the measurement.

The viscosity increased with the content of the quaternary ammonium unit. This was the consequence of the attraction between ion pairs. However, the interaction seems relatively weak, and

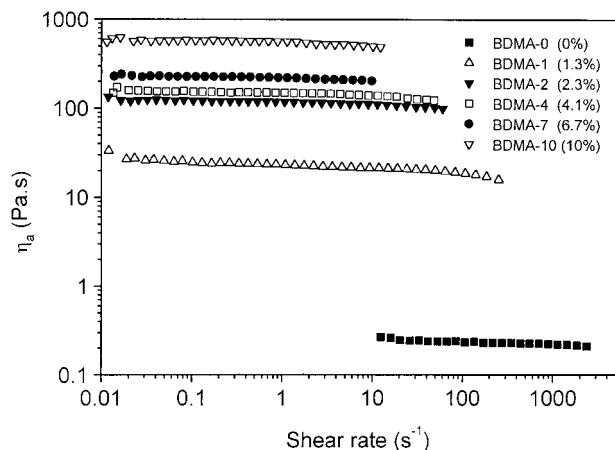


Figure 5 Viscosity versus shear rate at 20°C for the polysiloxane ionomers. The molar percentage of the quaternary ammonium chloride is shown.

the chain movement is not restricted. If the attraction between ion pairs were comparable with the level of the stress applied in the rheological measurement, or the structure change caused by flow could not be recovered rapidly, a non-Newtonian diagram would be obtained.

The γ -silylpropyl benzyl dimethyl ammonium cation and the chlorine anion are large ions. Therefore, the ion-ion attraction in the polysiloxane ionomers is relatively weak. The movement of the polymer chain in the ionomers must be quite

Table III Activation Energies for Viscous Flow of the Polysiloxane Ionomers

Sample Number	Ionic Unit Content (mol %)	ΔE_{η} (kJ mol ⁻¹)
BDMA-0	0	8.2
BDMA-1	1.3	46
BDMA-2	2.3	51.5
BDMA-4	4.1	49.6
BDMA-7	6.7	48.2
BDMA-10	10.0	48.2

easy at a temperature 40°C above the T_g of the cluster phase.

The effect of temperature on the viscosity of the polysiloxane ionomers at constant shear rate is shown in Figure 6. In the temperature range from 10 to 85°C, the relation between viscosity and temperature agreed very well with the Arrhenius equation. On the basis of the Arrhenius equation, the activation energies (ΔE_{η}) for viscous flow were calculated (see Table III).

The activation energy for flow is relevant to the intermolecular attraction of a fluid. It is seen that the ΔE_{η} of the parent poly(γ -chloropropylmethylsiloxane-*co*-dimethylsiloxane) is very low because of the chain flexibility and the low intermolecular attraction. There was a substantial increase in the activation energy of flow as the ionic units

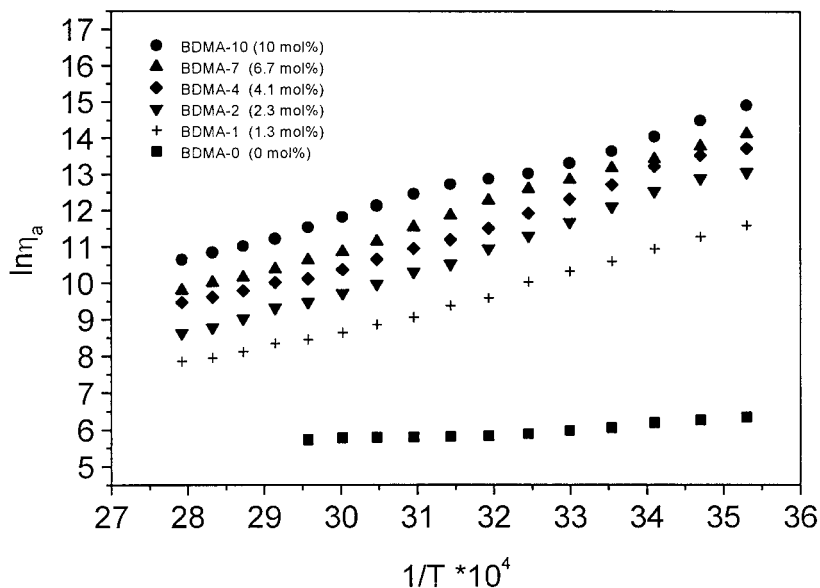


Figure 6 Temperature dependence of the viscosity for polysiloxane ionomers. The molar percentage of the quaternary ammonium chloride is shown.

were introduced. The ΔE_{η} was largely independent of the content of the ion unit, when the latter was above 2.3 mol %.

CONCLUSION

It was found that there existed ion clusters dispersed in the polysiloxane matrix when the concentration of the quaternary ammonium groups exceeded a critical value. The glass transition temperature of the ion clusters was found in the range of -20°C to -40°C . The cluster domains were visible at room temperature under TEM when the content of the quaternary ammonium chloride was above 2.3 mol %. The ionomers behaved as Newtonian fluid at room temperature. The flow activation energy was independent of the content of the ion unit when the latter was above 2.3 mol %.

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