Electrorheological Behavior of Side-chain Polysiloxane Containing 3-(4-Amidophenyl) Sydnone Moieties

Hua Yan[1], Wing Lai Chan[2], Yau Shan Szeto[3]

[1]Department of Petrochemistry, Logistic Engineering University, Chongqing, People's Republic of China
[2]Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Kowloon, Hong Kong, People's Republic of China
[3]Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Kowloon, Hong Kong, People's Republic of China

ABSTRACT: Side-chain polysiloxane containing 3-(4-amidophenyl) sydnone moieties at terminal and aliphatic spacer has been synthesized and its structure was confirmed by FTIR and ^{1}H-NMR. Low mass molar weight sydnone exhibited electrorheological effect, which was enhanced by electron-donor substituted group at phenyl, but weakened by electron-acceptor substituted group. By introducing sydnone into polysiloxane, the polymer displays the higher electrorheological effect due to the increased interaction between sydnone molecules. The oxide states of sydnone affect the electrorheological effect as well as the color of the product. Moreover, the temperature is higher than the glass transition temperature of the polymer; the electrorheological fluids show a very large leakage current. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2523–2528, 2004

Key words: polysiloxanes; rheology; conjugated polymers; stimuli-sensitive polymers

INTRODUCTION

Electrorheological fluids (ERF) are suspensions of polarizable particles in insulating oil, which exhibited a dramatic change in rheology in the presence of an electric field.[1–3] Thereby, controllable viscosity, yield stress, fast response, reversibility, and the simplicity of engineering designs using ERF have facilitated the development of many devices, such as auto dampers, active engine mounts, clutch valves, and servo devices.

Earlier studies on the ERFs covered various materials. Those hydrous ERFs have significant limitations and low electrorheological effects, which were associated with the presence of water. From 1988, dry base systems were employed in ERFs, which exhibited higher yield stress and were used in broad temperature ranges. Among various anhydrous ERFs, the dispersed phase materials have recently focused on conjugated polymer,[4–7] because some drawbacks of conductive polymer become advantageous for ERF. Moreover, their physical and chemical properties can be modified by acid or base to maximize the electrorheological effect.[8]

Sydnone is a kind of nonbenzenoid aromatic heterocyclic compound, called mesoionic compound, which cannot be represented satisfactorily by any one covalent or polar structure and possesses a sextet of electrons in association with the atom comprising the ring. The ring bears a fractional positive charge balanced by a corresponding negative charge located on a covalently attached atom or group of atoms.[9,10] The chemical and physical properties of sydnone and its derivatives have attracted significant interest due to their unique electronic structure and biological activity.[11–14]

For the unique molecular structure, sydnone possesses both conjugate and ionic characteristics, which make it sensitive both to electric and to magnetic fields, so it is possible to be used as dispersed phase material in ERFs. Besides the polarization of the particles, their interaction is also important for electrorheological behavior. A stronger interaction could be obtained if the sydnone moieties were attached to polymer. In this paper, we report the synthesis of polysiloxane containing 3-(4-amidophenyl) sydnone moieties and investigate the electrorheological behavior of several sydnones and the polysiloxane as functions of electric field strength, shear rate, particle concentration, and temperature by rotational rheometer with a high-voltage generator.

### Experimental section

Materials for synthesis

Poly(methylhydrosiloxane) (PMHS) was purchased from Acros, average molecular weight is from 2700 to 5400. Poly(dimethylsiloxane) (PDMS) was purchased from Chenguang Chemical Industry (Sichuan,China); the density and kinematic viscosity at 25°C were 0.960g/mL and 50 cST, respectively. Ethyl undecylenate (EU) is from Aldrich. Dichloro(dicyclopentadieny) platinum(II) (Cp_2PtCl_2) was from Strem Chemicals. Methanol, NaOH, active carbons, and HCl were

used as received, with no further purification. Toluene and tetrahydrofuran (THF) were dried and refluxed with sodium, used fresh.

Technology for characterization

^{1}H-NMR spectroscopy was performed on a Bruker DP X-400 with CDCl$_3$, acetone, and DMSO-d6 as solvent, respectively. FTIR spectra were recorded on a nicolet avatar 360 FTIR spectrometer; samples were prepared by compressing disks of KBr in case of solid or scribbling on KBr disks in case of liquid. Differential scanning calorimetry (DSC) was carried out using a Perking-Elmer DSC-7 differential scanning calorimeter at a heating or cooling rate of 10°C/min. Electrorheological behavior characterization was carried out using a rotational rheometer (NXS-11A, Instrument of Chengdu) with a high-voltage generator.
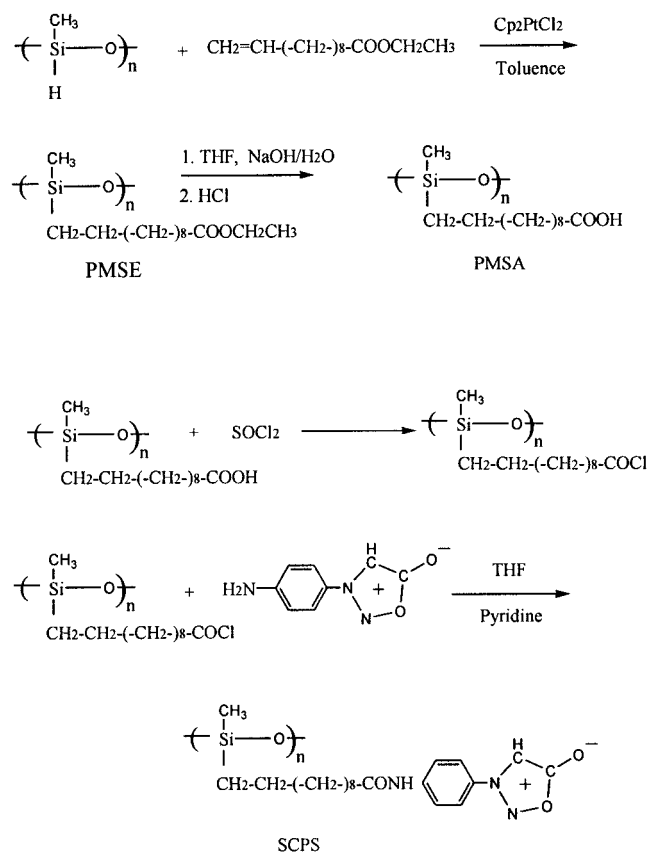
Hydrosilylation of PMHS and EU

To a 100-mL three-necked flask equipped with a reflux condenser, magnetic stirrer was added 1.6 g PMHS (25.6 mmol of Si–H units), 5.98 g EU (28.1 mmol), and 60 mL of dry, freshly distilled toluene. The reaction mixture were heated under nitrogen for 1 h at 110°C. Cp$_2$PtCl$_2$ (2.55 mg), in 4 mL dry, freshly distilled toluene, was injected with syringes. The reaction mixture was refluxed at 110°C and stirred under nitrogen for about 60 h. The reaction was monitored by observing

the disappear of Si–H at 2,167 cm^{-1} in FTIR and 4.72 ppm in ^{1}H-NMR. After reaction, 1.5 g active carbon was added and then filtered. The filtrate, dropped in 500 mL methanol, collected the product by centrifugation at 2500 rpm for 30 min. The final product is a light yellow viscosity liquid (5.5 g, yield 80%). ^{1}H-NMR (CDCl$_3$, δ in ppm): 4.14 (COOCH$_2$), 2.28 (CH$_2$COO), 1.61 (CH$_2$CH$_2$COO), 1.26((CH$_2$)$_7$), 0.50 (Si–CH$_2$),0.05 (Si–CH$_3$, CH$_2$CH$_3$). IR: (CH$_2$)$_7$ 2,975 cm^{-1}, C=O 1,733 cm^{-1}.

Hydrolysis of PMSE

PMSE (5.4 g; 19.64 mmol) was dissolved in 120 mL THF, and then 150 mL aqueous NaOH solution containing 1.573 g of NaOH (39.32 mmol) was added. At once, the solution became turbid. After heating at 65°C and stirring for 24 h, the solution became clear, indicating that the ester had been converted into COONa group, giving a product that is soluble in aqueous NaOH solution. After stopping the stirring and cooling processes, the mixture segregated into two cleaning layers. Vaporizing THF at vacuum, 1M HCl was added to acidify the COONa group. The resulting light yellow solid was washed with I.D. water and dried under vacuum at 55°C for 24 h (4.56 g, yield 80%). ^{1}H-NMR (DMSO-d6, δ in ppm): 2.16 (CH$_2$COO), 1.47 (CH$_2$–CH$_2$COO), 1.23 ((CH$_2$)$_7$), 0.48 (Si–CH$_2$), 0.08 (Si–CH$_3$). IR: 1,708 cm$^{-1,}$ C=O.

Synthesis of side-chain polysiloaxane containing of sydnone (SCPS)

PMSA (1.517 g; 5.519 mmol) was dissolved in 15 mL thionylchlorid, refluxed at 68°C for 2 h moisture-free. Afterward, thionylchlorid was extracted with vacuum, and 20 mL of dry and freshly distilled THF was added. Amidophenyl sydnone (APS; 0.9778 g; 5.519 mmol) was dissolved in 80 mL of dry and fresh THF and 10 drops of pyridine was added. At room temperature and while stirring, the THF containing acyl chloride was dropped into the THF solution containing APS. The yellow solid appeared about 30 min later, and the reaction continued to react overnight. The color of the solid was changed with the pH of solution. Because of the presence of pyridine, the solution is basic and the product was yellow. With the reaction, pH decreased due to the formation of HCl, and the product displayed a green color. The solid was dissolved in DMSO and then dropped into methanol to eliminate the excess APS and pyridine. The yellow solid was get after filter and dry at vacuum (1.77g, yield 73.89%). ^{1}H-NMR (DMSO-d6, δ in ppm): 10.32 (CONH), 7.85 (4H in phenyl), 7.67 (1H in sydnone), 2.33 (CH$_2$CONH), 1.57 (CH$_2$CH$_2$CONH), 1.23((CH$_2$)$_7$), 0.48 (Si–CH$_2$), 0.02 (Si–CH$_3$). IR: 1,744cm$^{-1,}$ C–O in sydnone, 2,922 cm^{-1}, C–H in sydnone.

Preparation of the ERFs

Electrorheological fluids were prepared by dispersing the grinded samples, such as phenylsydnone (PS), nitro-phenylsydnone (NPS), APS,[14,15] and SCPS in PDMS, which was dried in a vacuum oven and stored with molecular sieves before use. The mixture was grinded in muller for 10 min to disperse uniformly the particles in oil.

RESULTS AND DISCUSSION

Preparation of side-chain polysiloaxane

Momoner of sydnone cannot hydrosilylate with PMHS directly due to the complex between platinum catalyst and sydnone, so the introduction of sydnone into polysiloxane only can be amidated of acyl chloride with APS. The reaction was conducted at room temperature and was moisture free. With the reaction, the amide was produced unsolved in THF and precipitated from solution. When the reaction was performed, the pH of the solution decreased due to the production of HCl and the color of final product changed with the pH, displaying yellow at basic or neutral and green at acidic. For phenyl sydnone, its color is violet at acidic and displays green at neutral or basic. So, the wavelength of color of sydnone and its derivatives was shifted to a longer wavelength with increasing pH. Tien and Hunsberger[16] synthesized the 3-(3-pyridine)sydnone, which has photochromism. As we know, the color change of the polysiloxane containing mesoionic compound with the pH of solution was first reported by our group.

The ^{1}H-NMR spectroscopy of the final product confirmed the structure of polysiloxane containing sydnone. The main characteristic is the appearance of the peak at 10.32 ppm associated with amide. For APS, the chemical shift of H in phenyl and sydnone were 7.56~6.70 and 6.03 ppm, respectively. For polysiloxane, they are 7.85 and 7.67 ppm. For the formation of amide in polysiloxane, it had a stronger ability to
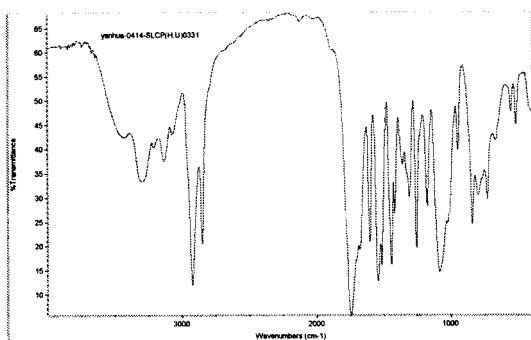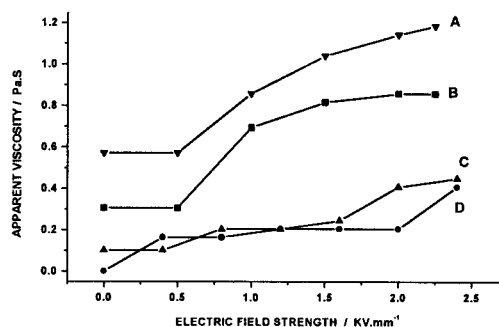

Figure 2 Electrorheological behavior of PS at different condition, (A) 25°C, 25wt%, 135.72 S^{-1}; (B) 25°C, 21wt%, 135.72 S^{-1}; (C) 40°C, 21wt%, 135.72 S^{-1}; (D) 25°C, 21wt%, 75.58 S^{-1}.

absorb electrons, and then made the chemical shift of H in phenyl and the sydnone shift to low field.

The FTIR spectrum also supports the structure of SCPS; see Figure 1. All amides are characterized by a strong carbonyl absorption band, referred to as the "amide I" band. Primary and secondary amides additionally show a band arising from N–H stretching and bending vibrations, it is generally at slightly lower frequency than the carbonyl absorption and is referred to as the "amide II" band. The asymmetric and symmetric stretching vibrations of the two N–H bonds in APS are 3,451 and 3,351 cm^{-1}. In SCPS, only the 3,301 cm^{-1}, due to one N–H bond in the secondary amide, appeared at its place. In the IR spectrum of APS, 1,743 cm^{-1} is the carbonyl absorption band, but, for SCPS, there are bands at 1,744 cm^{-1} and 1,682 cm^{-1}, respectively, which represent the absorption band of C=O and N—H.

Electrorheological behavior of sydnone and its derivatives

3-(4-Phenyl) sydnone is the model mesoionic compound, the sydnone ring bears a fractional positive charge balanced by a corresponding negative charge, and the dipole is sensitive to the electric field. Figure 2 shows the dependence of apparent viscosity on electric field strength for mixture of PS and PDMS at different temperatures, particle concentrations, and shear rates. The critical electric field strength for PS is 0.5 kV/mm at 25°C and 25 wt %, but with an increase of temperature or a decrease of shear rate, the critical electric field strength increases to 1.5~1.6 kV/mm. The apparent viscosity increases quickly around the critical electric field strength and then slows down. Moreover with the increased concentration of PS, the peak shifts to a higher electric field strength. Maybe there are satisfaction of polarization for sydnone compounds, which was related with the structure of sydnone.
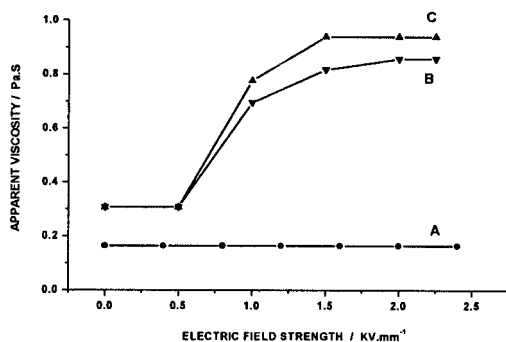

Figure 1 The FTIR spectrum of polysiloxane containing 3-(4-amidophenyl) sydnone.

Figure 3 Electrorheological behavior of differen sydnone derivatives, (A) NPS; (B) PS; (C) APS with condition of 21 wt %, $135.72S^{-1}$ and 25°C.

Figure 3 exhibits the effect of different mesoionic compounds on electrorheological behavior. APS shows the highest electrorheological effect, but NPS has little electrorheological effect. Electron-donor groups, such as CH_3, OCH_3, NH_2, and OH, push the electron to the phenyl and increase the density of electron cloud, so the polar–polar interaction increases as well as the polarization of the particle at the electric field, and the mixture of APS/PDMS displays the highest apparent viscosity. But the substitute group was replaced by nitro, which is the electron-acceptor group, bringing on the decrease of density of the electron cloud in the conjugated system and the mixture of NPS/PDMS exhibits the lower electrorheological effect.

Electrorheological behavior of polysiloxane containing sydnone

As we know, electrorheological behavior was associated with polarization of particles, migration of charge, and formation of columns.[17] Besides the polarization of particles, the interaction of them is also important for electrorheological effect. So, the small electrorheological effect of the low molar weight sydnone may be attributed to the weak interaction between sydnones or their group induced under an electric field and a stronger interaction could be obtained if the sydnone moieties were attached to the side chain of the polymer. On this assumption, the sydnone was introduced into polysiloxane to improve the electrorheological effect.

Figure 4 shows the apparent viscosity of the sydnone, its derivatives, and polysiloxane containing sydnone. As the sydnone was linked to polysiloxane, apparent viscosity of the side chain polysiloxane is higher than that of low molar weight sydnone with no electric field present. Just as assumed, the polysiloxane containing sydnone displays a stronger electrorheological effect in the presence of the electric field. The apparent viscosity of polysiloxane is increased greatly

compared with PS and APS. However, purified polysiloxane has little electrorheological effect.

Polysixloxane containing sydnone was synthesized by amidation of acyl chlorde with APS at room temperature and moisture free in the presence of pyridine. With performing of reaction, the pH of the mixture decreases due to the production of HCl. The product was purified by dissolving it into DMSO and precipitating into methanol. So the stronger electrorheological effects of polysiloxane containing sydnone were associated with a hybrid as well as attaching to polysiloxane. Besides the difference in structure, the hybrid is an important reason for electrorheological behavior. As we know, just like mesoionic compound, the sydnone and it derivatives have an unusual electrical structure, so the acid or base in synthesis and purification could affect their electrical properties. In acid, the interaction of H^+ and O^- made the center of positive and negative charges elongate and the polarity of sydnone increase, so it shows the greater electrorheological effect. But in neutral and base, the exclusion of OH^- and O^- made the center positive and negative charge shrink and the polarity of sydnone decrease, so the electrorheological effect was lessened.

Just like other semiconducter polymers, the color of product was changed with the pH of aqueous. In the synthesis process, due to the presence of pyridine, the solution was basic and the product was yellow. With the reaction, pH decreased due to the formation of HCl and it becomes a green solid. When the green solid was treated with base or water, it changed into yellow again. On the same assumption, the physical and chemical properties can be modified by acid or base to maximize the electrorheological effect. Unfortunately, the product treated with base or acid didn't exhibit the stronger electrorheological effect, some change maybe happen in sydnone ring treated with inorganic acid or base.

Figure 5a shows the dependence of apparent viscosity on electric field strength for the mixture of polysi-
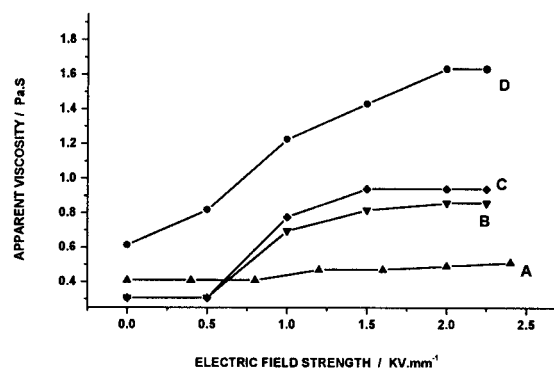

Figure 4 Electrorheological behavior of (A) purified SCPS, (B) PS; (C) APS and (D) SCPS at condition of 25°C, 21wt%, $135.72S^{-1}$.
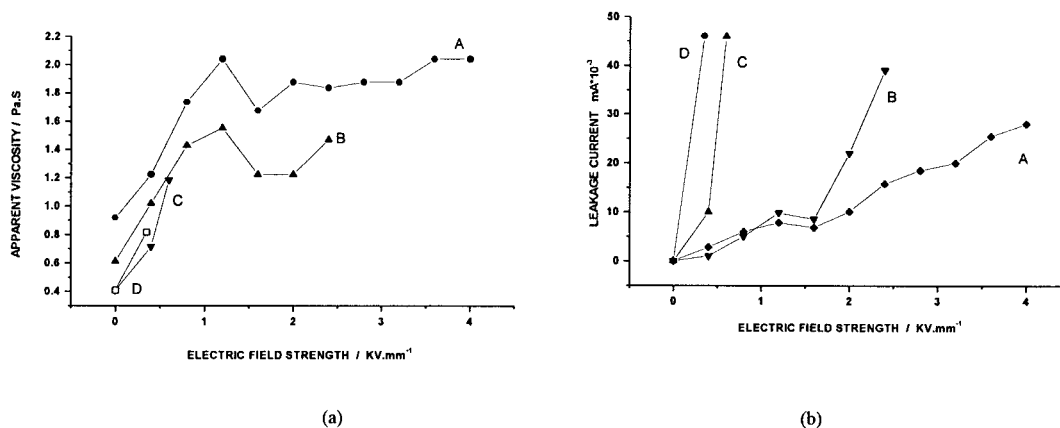
Figure 5 Apparent viscosity (a) and leakage current (b) of mixture of SCPS and PDMS at different temperature (A) 22°C; (B) 40°C; (C) 60°C and (D) 74°C with the condition of $135.72S^{-1}$ and 21wt%.

loxane containing sydnone and PDMS at different temperatures. The effect of temperature on the electrorheological effect exhibited two sides. On the one hand it enhanced the electrorheological effect by increasing permittivities with temperature; on the other hand, the viscosity of mixture decreased with increasing of temperature. Under 60°C, the effect of viscosity exceeds the effect of permittivities, so the apparent viscosity decreased with increasing temperature. When temperature reached 74°C, the effect of permittivities becomes stronger. The apparent viscosity at 74°C is higher than that of 60°C and shows a large leakage current at same electric field strength.

Figure 5-b is the curve of leakage current via electric field strength at different temperature. With the increasing of temperature, leakage current increasing rapidly after 60°C, this change become very sharp. Generally, the relationship of conductance of conduct polymer and temperature is exponent, whether it is conducted in electron or in ionic. With the increasing of temperature, the concentration of conduct carrier become higher in polymer, so the conductance result the large leakage current. On the other hand, conduc-
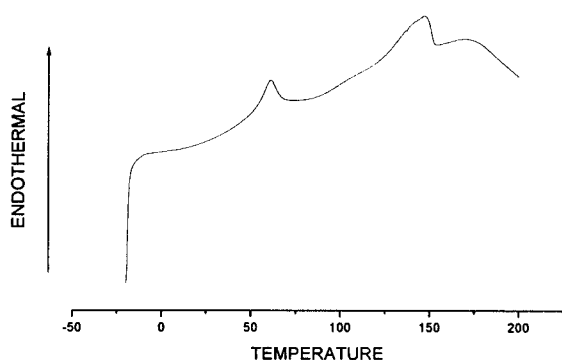
tance of conduct polymer changes greatly around the glass transfer temperature. From the DSC curve of polysiloxane (see Fig. 6), its glass transfer temperature is 70°C. The polymer chain becomes very active after Tg, which results the increasing of migration rate of ionic particle. For the two reasons, the leakage current of the ERF becomes very large.

CONCLUSION

A new class of side chain polysiloxane containing the mesoionic compound, such as sydnone group, has been synthesized. The structure of the polysiloxane was confirmed by FTIR and ^{1}H MNR. Due to the complexed of platinum catalyst and sydnone, the olefinic derivative containing sydnone can not been introduced into polysiloxane by hydrosilylation.

For the unique structure of sydnone, the PS exhibited electrorheological effect, which was enhanced by replaced the electron-donor group at phenyl, but was weakened by electron-acceptor group. Attached the Sydnone to the side chain of polysiloxane, the polymer display higher electrorheological effect due to enhanced of interaction of sydnone. Moreover, the electrorheological effect related with the oxide state of sydnone, so the purificated sample has hardly electrorheological effect. By increasing of temperature there are the effect of viscosity and of permittivities, which related to the electrorheological effect. If the temperature is higher than Tg of polymer, the ERF display very large leakage current.

Figure 6 The DSC thermogram curve of polysiloxane containing sydnone.

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