

Synthesis and Comparative Properties of Poly(dimethylsiloxane) Grafted Alkyl Acrylate

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ABSTRACT: Low hydrogen-containing siloxane (*l*-PDMS) material was prepared by H₂SO₄-catalyzed equilibration of octa-methyl cyclo tetra siloxane (D4), hexamethyl disiloxane (MM) and high hydrogen-containing siloxane (h-PDMS). Poly(dimethylsiloxane) (PDMS) grafted methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) were prepared by Pt-catalyzed hydrosilylation reaction of *l*-PDMS and three acrylates, respectively. PDMS grafted alkyl acrylate not only preserves the properties of PDMS, but also adds new ones. Viscosity, viscosity-temperature coefficient (VTC), viscosity-index (VI), and TGA experiments indicate that the grafted copolymers have outstanding thermal stabil-

ity as PDMS. The measurement of surface tension (ST) shows the grafted copolymers have low surface energy as PDMS. However, emulsifiability, lubricity, and solubility in organic solvent, such as acetone, isopropanol, of PDMS grafted alkyl acrylate were better than the properties of PDMS, which can be very useful for fine chemical industry. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3600–3604, 2007

Key words: alkyl acrylate; poly(dimethylsiloxane); synthesis; visco-temperature characteristics; surface tension; thermal stability

INTRODUCTION

The copolymers containing poly(dimethylsiloxane) (PDMS) have received considerable attention. They have unique properties, such as very low glass transition temperature, remarkable high-low temperature resistance, low surface energy, and physiological inertness.^{1–3} Some of their specialty applications are in the fields of mechanical industry, chemical industry, building industry, and even biomedical industry. These copolymers have been prepared into a wide variety of surfactants, such as lubricating oil, wetting, waterproofing, leveling agent, and antifoam.^{4–7}

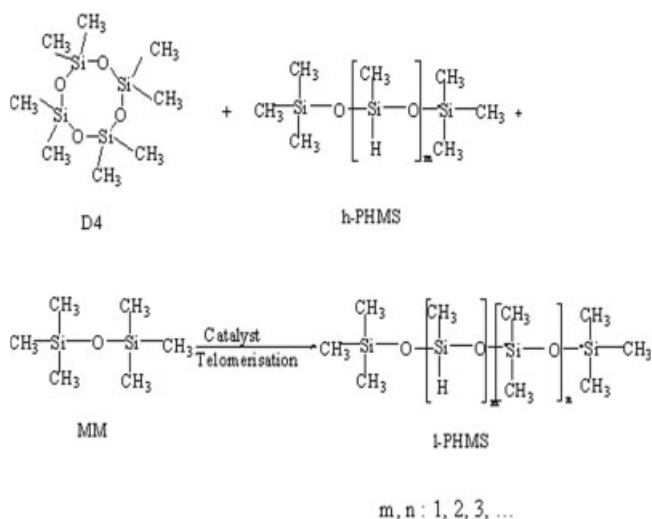
However, the properties of the copolymers containing PDMS depend on the kinds of grafting groups as well as the molar ratio of two components. Definitely, different grafting groups endow the copolymers different properties. For example, epoxy group gives the copolymers reactivity and flexibility; polyether brings to the copolymers water solubility, water dispersibility, and emulsibility; alkyl acrylate in this article gives the copolymers novel acidic and alkali resistance, outstanding solubility in organic solvents and organic polymers.^{8–10} The greater the molar ratio of grafting groups, the more distinct chemically modified effect, so distinct that even the copolymers lose

the special characters of PDMS, such as very low glass transition temperature, remarkable high-low temperature resistance, low surface energy, and physiological inertness.^{11,12}

In this article, we synthesized PDMS grafted alkyl acrylate via two well-known and commonly used reactions. Equilibration of polysiloxane was used to prepare low hydrogen-containing siloxane (*l*-PDMS).¹³ Hydrosilylation was used to synthesize PDMS grafted alkyl acrylate. FTIR and ¹H NMR spectra characterized the structures of the grafted copolymers.^{14,15} Properties of the grafted copolymers such as viscosity, viscosity-temperature coefficient (VTC), viscosity index (VI), surface tension (ST), thermal stability, and solubility were tested. In the end, we studied the relation between the structures and the properties of polysiloxanes with carboxylic esters pendant to polysiloxane chains, and compared the properties of the PDMS grafted alkyl acrylate.

In previous work,^{16–21} and the study in this article, PDMS grafted alkyl acrylate has good physical and chemical properties, for example, low VTC and high VI suggest that the copolymers have a low viscosity variation with temperature; low ST shows the copolymers has low surface energy. Taking advantage of these characters, we can develop different kinds of products that have broad applications, such as application of leveling and wetting agent in coating industry; application of antifoam in textile, fermentation, and petroleum industry; application of regulator and control agent in synthesis of rubber and resin.

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Scheme 1 Mechanism of telomerization reaction with h-PDMS.

EXPERIMENTAL

Materials

Methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) were first distilled from CaC_2 , followed by distillation from triethyl aluminum. Octa-methyl cyclo tetra siloxane (D4), hexamethyl disiloxane (MM), and high hydrogen-containing siloxane (h-PHMS) were obtained from DOW CORNING Company.

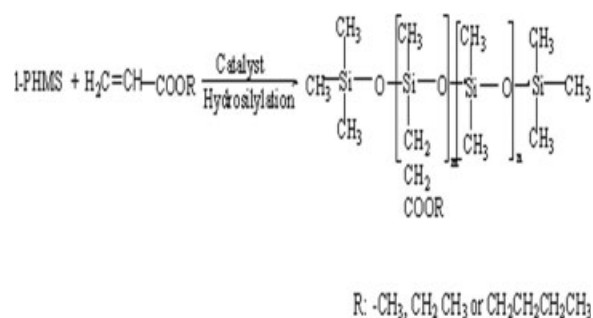
Hydrosilylation catalyst, platinum chloride isopropanol solution, was made according to the following procedure: fed 0.5 g Pt into 100 mL isopropanol, and the resulting liquid in light yellow was preserved in dark and dry place.

Characterization methods

IR spectra were recorded via a Mattson Galaxy 3000 FTIR spectrophotometer. ^1H NMR spectra was obtained with a Bruker AM 500 NMR spectrometer operating at 500 MHz. Viscosity of copolymers was measured on a NDJ-79 Rotating viscometer, viscosity-temperature coefficient (VTC), VI, and ST were carried out according to the Chinese standards of GB/T 1990-5549, GB/T 1995-88, and HG/T 236, respectively. Thermogravimetric analysis experiments were conducted with a Perkin-Elmer Pyris 1 TGA on samples ranging from 10 to 15 mg, at a heating rate of $10^\circ\text{C}/\text{min}$.

Preparation of low hydrogen-containing siloxane (l-PHMS)

Telomerization reaction was conducted in a dried 500 mL-round bottom flask equipped with a mechanical stirrer, a temperature controller, and a water con-



Scheme 2 Mechanism of hydrosilylation reaction of PDMS and acrylate.

denser. D4, h-PHMS, and MM were added into the reaction flask with stirring. The reaction was allowed to proceed for 4 h at 80°C in the presence of concentrated sulfuric acid as catalyst (Scheme 1). Then the pH was adjusted to 7 with anhydrous sodium carbonate, and the precipitate was filtered.

Preparation of MA, EA, and BA grafting PDMS, respectively

Hydrosilylation reaction was conducted in a dried 500 mL four-neck round bottom flask equipped with a

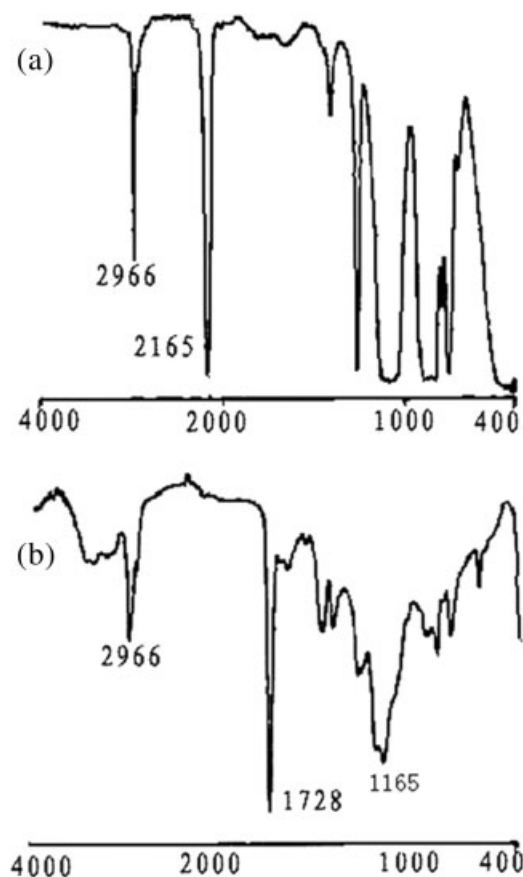


Figure 1 Infrared spectrum of l-PHMS and grafted copolymer: (a) l-PHMS, (b) grafted copolymer.

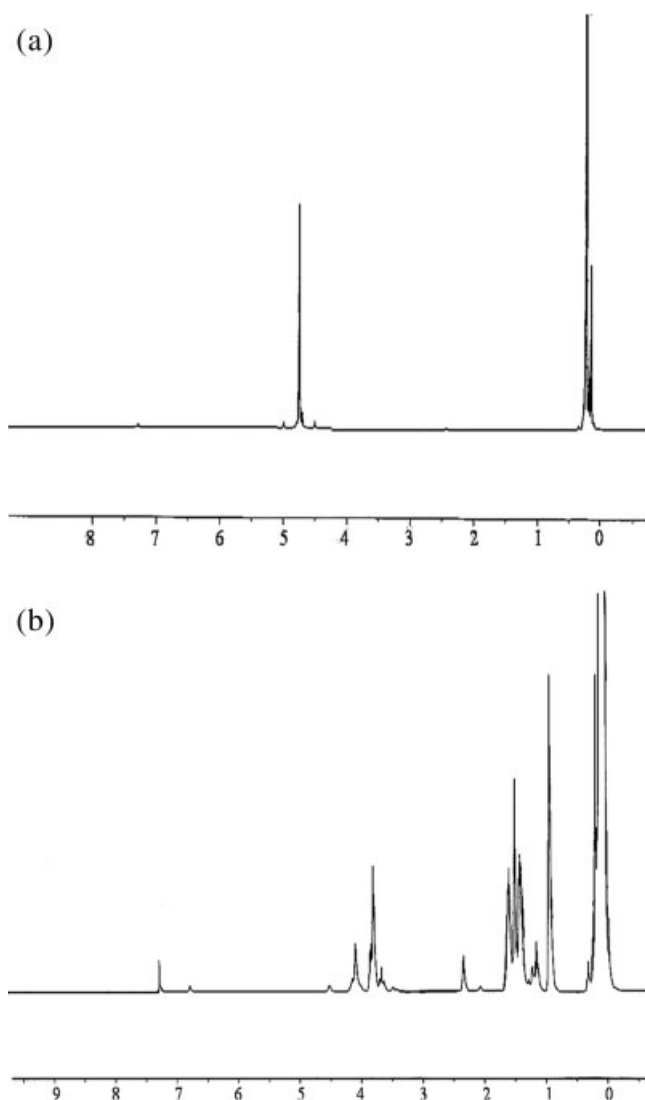


Figure 2 ^1H NMR spectra of *l*-PHMS and grafted copolymer: (a) *l*-PHMS (b) grafted copolymer.

mechanical stirrer, a temperature controller, and a water condenser. *l*-PHMS and acrylate were fed into the reaction flask. With stirring, under nitrogen atmosphere, the reaction was allowed to stand for 1 h at 90°C in the presence of platinum chloride as catalyst (Scheme 2). Then the reaction mixture was distilled under reduced pressure to remove the low boiling components.

RESULTS AND DISCUSSION

FTIR spectroscopy analysis of *l*-PHMS and grafted copolymers

Structural changes of grafted copolymers are shown in Figure 1. The strong peak at 2165 cm^{-1} is due to the stretching vibration of Si—H [Fig. 1(a)]. The strong peak at 1728 cm^{-1} and the medium peak at 1165 cm^{-1} are attributed to C=O and C—O, respectively, [Fig.

1(b)], indicating the presence of acrylate groups. The disappearance of Si—H absorption peak in Figure 1(b) suggests that PDMS has been grafted by acrylate through hydrosilylation reaction of *l*-PDMS with MA, EA, and BA, respectively.

^1H NMR spectroscopy analysis of *l*-PHMS and grafted copolymers

Structural differences between *l*-PHMS and grafted copolymer are shown in Figure 2. Comparing the two spectra, we can find that the strong vibration absorption at $\delta: 4.72$ is attributed to Si—H [Fig. 2(a)]. But the two absorptions both disappear in Figure 2(b), the vibration absorption peaks of $\text{Si}(\text{CH}_2\text{CH}_2\text{COOR})\text{CH}_3$, Si CH_2 , CH_2CH_3 , CH_2CH_3 , $\text{CH}_2\text{CH}_2\text{CH}_3$, CH_2CO , and OCH_2 appear at $\delta: 0.12$, $\delta: 0.20$, $\delta: 0.90$, $\delta: 1.41$, $\delta: 1.51$, $\delta: 2.00$, and $\delta: 4.10$ [Fig. 2(b)], respectively. Appearance of these peaks proves that PDMS has been grafted by MA, EA, and BA, respectively.

Study on visco-temperature characteristics of grafted copolymers

The relation between viscosity and temperature of grafted copolymers is shown in Figure 3. With the increase of temperature, the viscosities of graft copolymers decline. The viscosity of BA-*g*-PDMS is the highest in the grafted copolymer followed by that of MA-*g*-PDMS with the viscosity of EA-*g*-PDMS being lowest at the same temperature. This is because the viscosity of copolymers has a relation with the microstructures and intermolecular forces. Intermolecular forces of BA-*g*-PDMS are the greatest, so its viscosity is the highest; intermolecular forces of EA-*g*-PDMS are little greater

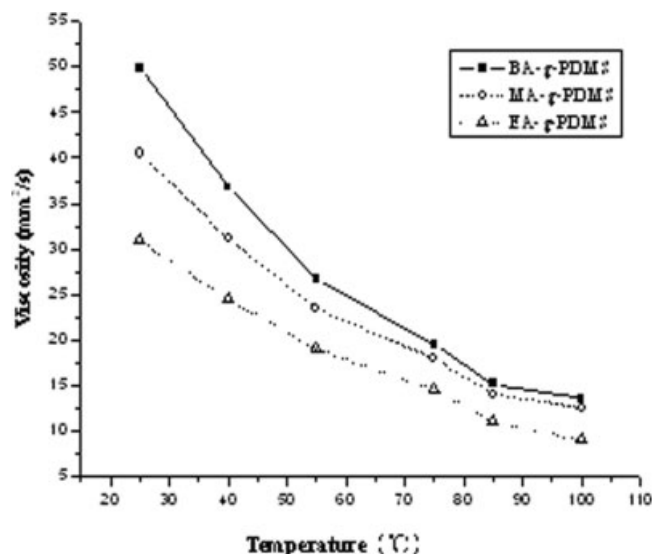


Figure 3 Viscosities of graft copolymers. The copolymers were synthesized by *l*-PHMS: hydrogen content was 0.12% and viscosity was $40\text{ mm}^2/\text{s}$ at 25°C.

TABLE I
VTC and VI of Grafted Copolymers

Polymers	VTC	VI
MA-g-PDMS	0.59–0.66	354–420
EA-g-PDMS	0.61–0.69	342–412
BA-g-PDMS	0.61–0.72	338–400

The copolymers were synthesized by *l*-PHMS: hydrogen content was 0.01–0.20% and viscosity was 20–60 mm²/s at 25°C.

than those of MA-g-PDMS, but polarity of MA-g-PDMS is much stronger than that of EA-g-PDMS; strong polarity of MA set off the viscosity reduction result from intermolecular forces, induced the viscosity of MA-g-PDMS is much higher than viscosity of EA-g-PDMS. As a result, the viscosity of MA-g-PDMS is much higher than that of EA-g-PDMS.

The VTC and VI of grafted copolymers are listed in Table I. It shows that the VTC of MA-g-PDMS is the least, and the VI of MA-g-PDMS is the greatest. It suggests that the visco-temperature property of MA-g-PDMS is the best; VTC and VI of EA-g-PDMS and BA-g-PDMS are similar in Figure 3. It proves that the visco-temperature properties of EA-g-PDMS and BA-g-PDMS are similar.

Study on surface properties of grafted copolymers

Figure 4 shows the relation between the grafting percentage with MA, EA, and BA and the ST of grafted copolymers. With the increase of hydrogen, the ST of MA-g-PDMS, EA-g-PDMS, and BA-g-PDMS rise. The ST sequence of the grafted copolymers from low to

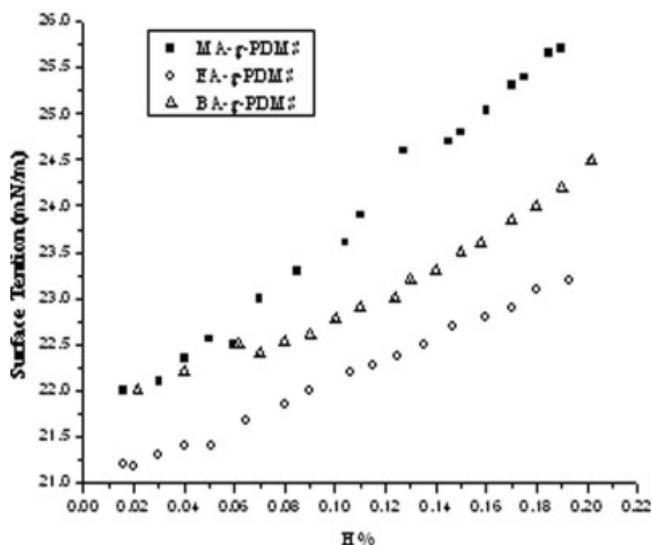


Figure 4 Surface tension of grafted copolymers. The copolymers were synthesized by *l*-PHMS: Hydrogen content was 0.01–0.20% and viscosity was 40 mm²/s at 25°C.

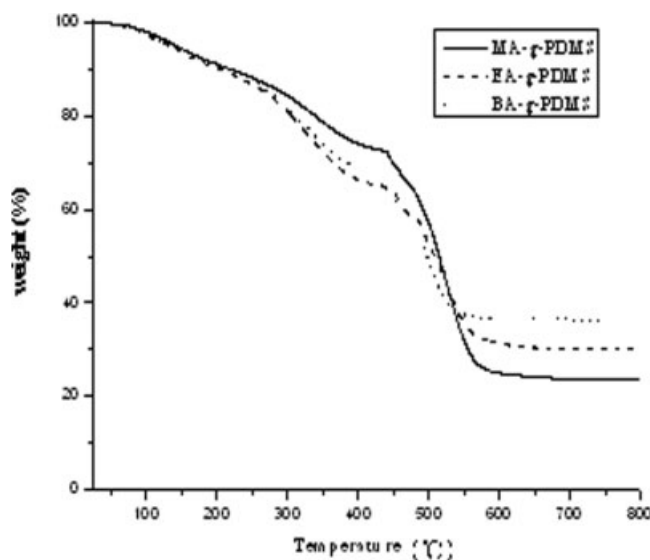


Figure 5 TGA thermogram of graft copolymers in nitrogen.

high is EA-g-PDMS, BA-g-PDMS, and MA-g-PDMS. The results are reasonable because ST is closely related to the microstructures of grafted polymers. Polarity sequence of three acrylates from low to high is MA, BA, and EA. Their local polarities prevent methyl circumvolving around Si—O—Si backbone. Consequently, the ST of grafted polymers increases.

Study on thermal stability of graft copolymers

Figure 5 gives the TGA curves for MA-g-PDMS, EA-g-PDMS, and BA-g-PDMS under nitrogen atmosphere. MA-g-PDMS, EA-g-PDMS, and BA-g-PDMS are thermally stable to only 142, 135, and 134°C, respectively. Above these temperatures, grafted copolymers degradation occurs in three stages. At 432°C, MA-g-PDMS, EA-g-PDMS, and BA-g-PDMS remains 73, 65, and 65%, respectively. The degradation in this procedure results from MA, EA, and BA decomposition. The final decomposition temperature of MA-g-PDMS, EA-g-PDMS, and BA-g-PDMS is 699, 697, and 696°C, respectively. The procedure results from PDMS decomposes. No additional weight is lost on heating the samples to 800°C. Among all the TGA curves, MA-g-PDMS is the most thermally stable, while EA-g-PDMS and BA-g-PDMS have the similar thermal stability.

Study on solubility

PDMS grafted alkyl acrylate is easy to dissolve in non-polar solvents such as PDMS. Its solubility becomes lower while its viscosity becomes higher. When the viscosity is 1000 mm²/s, they partly dissolve in carbon

tetrachloride. However, alkyl acrylate endows them new solubility character, so they can also dissolve in some polar solvents. Solubility becomes higher while the molar ratio of alkyl acrylate becomes higher. When the molar ratio is 0.001, they can dissolve completely in acetone and isopropanol.

SUMMARY

MA-*g*-PDMS, EA-*g*-PDMS, and BA-*g*-PDMS were synthesized by Pt-catalyzed hydrosilylation reaction. The structures of grafted copolymers were confirmed by ¹H NMR and FTIR spectroscopy.

Visco-temperature properties of the grafted copolymers are all fine. Especially, the VTC and VI of MA-*g*-PDMS are 0.59–0.66 and 354–420, respectively. ST sequence of the grafted copolymers with the same grafting percentage from high to low is MA-*g*-PDMS, BA-*g*-PDMS, and EA-*g*-PDMS, and all the grafted copolymers have low ST. The grafted copolymers also exhibit excellent thermal stability; the temperature for onset of degradation of MA-*g*-PDMS, EA-*g*-PDMS, and BA-*g*-PDMS is 142, 135, and 134°C, respectively. The copolymers have fine solubility, and they can dissolve in same polar solvents, which enlarge the application areas.

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