Journal of Applied Polymer Science

POEGMA-*b*-PAA comb-like polymer dispersant for Al_2 suspensions

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ABSTRACT: POEGMA-*b*-PAA comb-like polymer is synthesized through RAFT polymerization, and it is employed as an efficient dispersant for Al_2O_3 suspensions. The POEGMA-*b*-PAA polymer consists of PAA chains and POEGMA comb-like chains. The former provide electrostatic attraction between Al_2O_3 particles and polymer, while the latter extend to solution and maintain the stability of suspension due to strong steric hindrance. The adsorption is proven and the rheology behaviors of Al_2O_3 suspensions are strongly improved. Different POEGMA-*b*-PAA polymers with different length of side chains have similar but not identical rheological properties. The polymer with the appropriate length of side chain provides the biggest improvement to rheological properties of Al_2O_3 suspensions, such as apparent viscosity and granularity. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43352.

KEYWORDS: copolymers; rheology; viscosity and viscoelasticity

Received 29 October 2015; accepted 15 December 2015

DOI: 10.1002/app.43352

INTRODUCTION

Ultrafine alumina, which has a particle diameter less than 10 μm, have been widely used as a pivotal functional material in various fields, including catalysts and catalyst supports, separating applications, metallurgy due to its superior physical and chemical properties, such as high rigidity, high heat-resistance, good electrical resistivity, and so on.[1–3] Additionally, microcrystalline aluminas have been gradually used for producing Al_2O_3-based ceramics as a kind of precursor material.[34,35] In special, nanocrystalline aluminas, with a diameter less than 1 μm, were in research in recent years due to its outstanding specific surface area. However, ultrafine alumina, especially small-scale Al_2O_3 particles, is easily aggregated due to this ultrahigh surface area and energy. Different kinds of surfactant, therefore, have been developed and added to Al_2O_3 suspensions in order to solve the aggregation problem. Su *et al.*[4] reported alkylphenol ethoxylates (OP-10) as a non-ionic surfactant and a deflocculating agent in preparing α-Al_2O_3 powder. Polyethylene glycol (PEG) is another typical non-ionic dispersant, which was reported by Xu *et al.*[5] However, non-ionic surfactant is not able to keep the dispersion stability of Al_2O_3 suspension, which means Al_2O_3 particles aggregate after long time of storage. Later, Liu *et al.*[6] reported cetyltrimethyle ammonium bromide (CTAB) as a kind of ionic surfactant and Pham *et al.*[7] reported sodium dodecyl sulfate as another. Ionic surfactant can be absorbed onto the surface and provide electrostatic repulsion between Al_2O_3 particles, which leads to a better stability of Al_2O_3 suspensions. Among ionic surfactant, polyacrylic acid (PAA), as a representative of polyelectrolyte, is widely used as a dispersant for Al_2O_3 suspensions and proven to have outstanding dispersibility.[8–12] However, due to its simple molecule structure, it is difficult to further improve the dispersibility of PAA. Thus, we need to investigate a better structure to get a more efficient dispersant. Comb polymer, which is widely used in cement and concrete area, is a good candidate. Some comb-like copolymers have been developed as dispersants for SiO_2 suspensions,[13] $BaTiO_3$ suspensions,[14] and Al_2O_3 suspensions.[15–17] Ran *et al.*[18] reported poly(styrene-*co*-maleic anhydride) grafted methoxypolyethlene glycols (SMA-*g*-MPEG) for the dispersion of Al_2O_3 suspensions and improved its rheological properties.

New methods of controlled free-radical polymerization, such as nitroxyl-mediated polymerization[19–21] (NMP), atom transfer radical polymerization[22–24] (ATRP), and reversible addition-fragmentation chain transfer polymerization[24–27] (RAFT), have been developed and applied in synthesis process of polymers with certain structure. Among these techniques, we choose RAFT in this paper, not only for its convenience in controlling synthesis process, but for its unique environmental friendly characteristic of using aqueous solution as reaction medium.[28]

Additional Supporting Information may be found in the online version of this article.

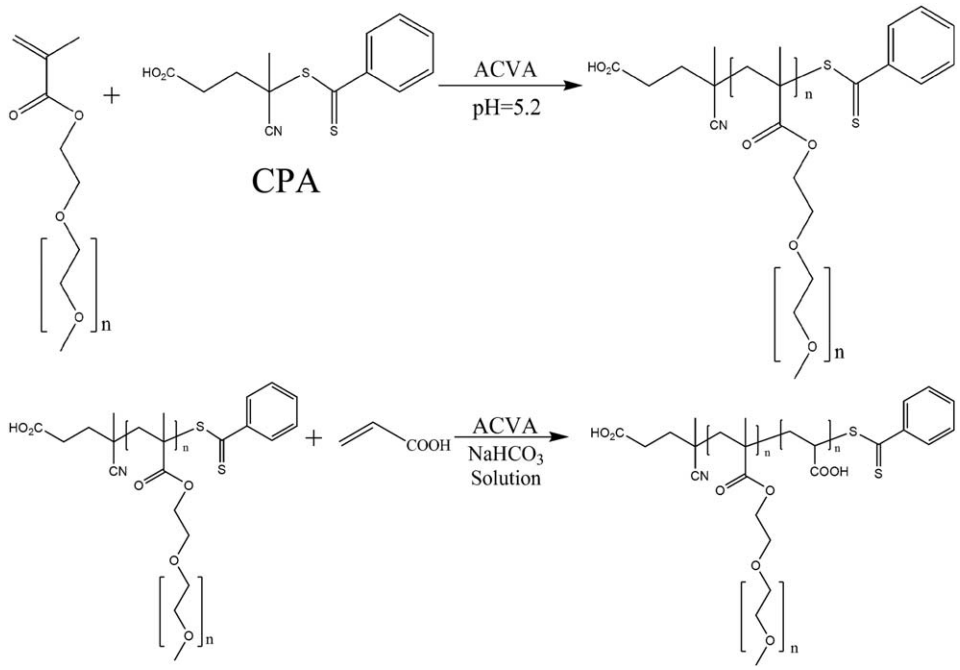

Figure 1. Synthesis of POEGMA-*b*-PAA.

Based on the ideas above, we design a novel comb-like block copolymer, poly(oligo(ethylene glycol) methyl ether methacrylate)-*block*-polyacrylic acid (POEGMA-*b*-PAA), which is successfully synthesized manageably and utilized as the dispersant for Al_2O_3 suspensions in this paper. Comparing with random copolymer, block copolymer offers a better structure designability and regularity, which makes it easier to find the copolymer with the best performance we need.[29,30] The POEGMA-*b*-PAA comb-like block copolymer is prepared through RAFT, using OEGMA with different molecular weight and acrylic acid as raw material, along with CPA as the RAFT chain transfer agent and ACVA as initiator, as shown in Figure 1. The POEGMA-*b*-PAA has two parts. One is the anionic polyacrylic acid chain, which can absorb onto the surface of Al_2O_3 particles. The other is the POEGMA comb-like chain, which can extend into solution and provide steric repulsion. The comb-like POEGMA-*b*-PAA is proven efficient in dispersing Al_2O_3 suspensions from the results below.

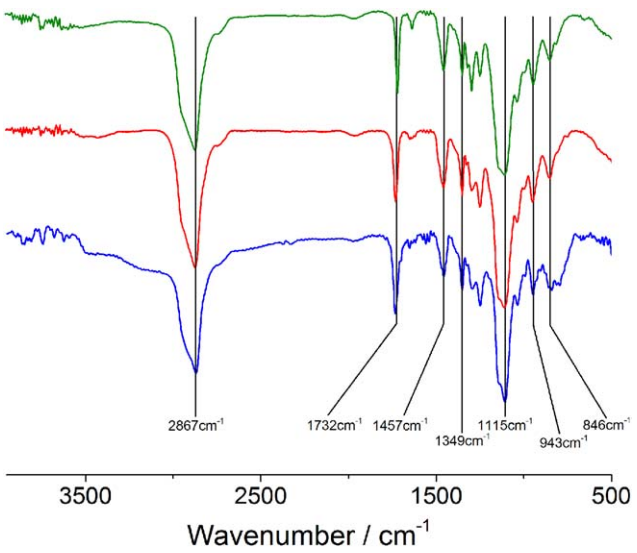

Figure 2. FT-IR spectra of $OEGMA_{950}$ (a), $POEGMA^{950}$ comb-CPA (b), and $POEGMA^{950}$-*b*-PAA (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Acrylic acid was purchased from Sinopharm Chemical Reagent Co., Ltd., and purified by distillation before use. Three different specifications of oligo(ethylene glycol) methyl ether methacrylate ($OEGMA^{500}$, number-average molecular weight $M_n = 500$ g/mol, $OEGMA^{950}$, number-average molecular weight $M_n = 950$ g/mol, and $OEGMA^{2000}$, number-average molecular

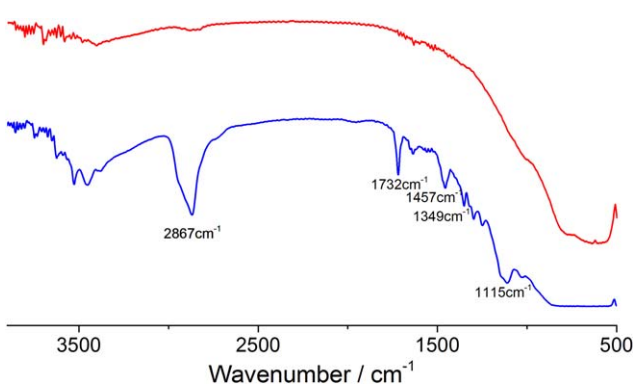

Figure 3. FT-IR spectra of Al_2O_3 (a) and Al_2O_3/$POEGMA^{950}$-*b*-PAA (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

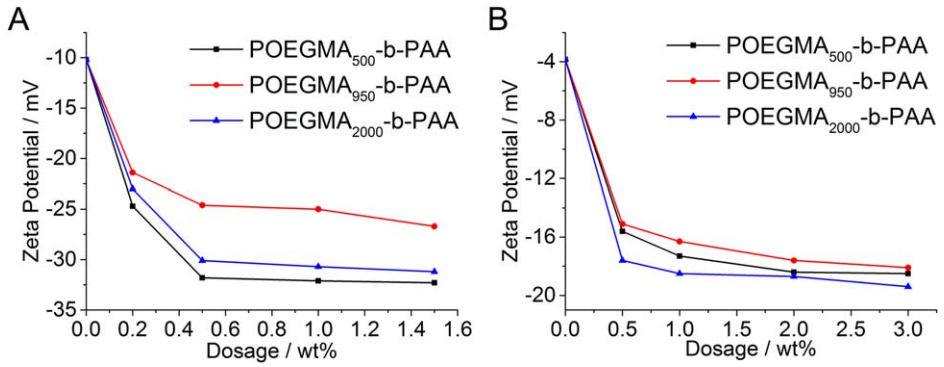

Figure 4. Effect of POEGMA-*b*-PAA on Zeta potential of Al2O3 (A) and Nano-Al2O3 suspension (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight $M_n = 2000$ g/mol) were both purchased from Aldrich, both in solution with a concentration of 50%. 4,4′-Azobis(4-cyanovaleric acid) (ACVA) and 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPA) were purchased from Aldrich. Acetic acid, sodium acetate, and $NaHCO_3$ were purchased from Shanghai Chemical Reagent Co, Ltd. Alumina powder was purchased from XuanCheng JingRui New Material Co., Ltd. The powder was produced through wet milling process without extra surface treatment. The average diameter labeled was 2.3 μm for ordinary Al_2O_3 powder and 150 nm for nano-Al_2O_3 powder.

Block Copolymerization

Synthesis of POEGMA Comb-CPA. To a three-necked flask equipped with a magnetic stir bar were added $OEGMA^{500}$/$OEGMA^{950}$/$OEGMA^{2000}$, CPA, ACVA, and excess 1*M* acetate buffer. The solution was purged with nitrogen for 30 min and then heated to 70°C under stirring in a thermostated oil bath.

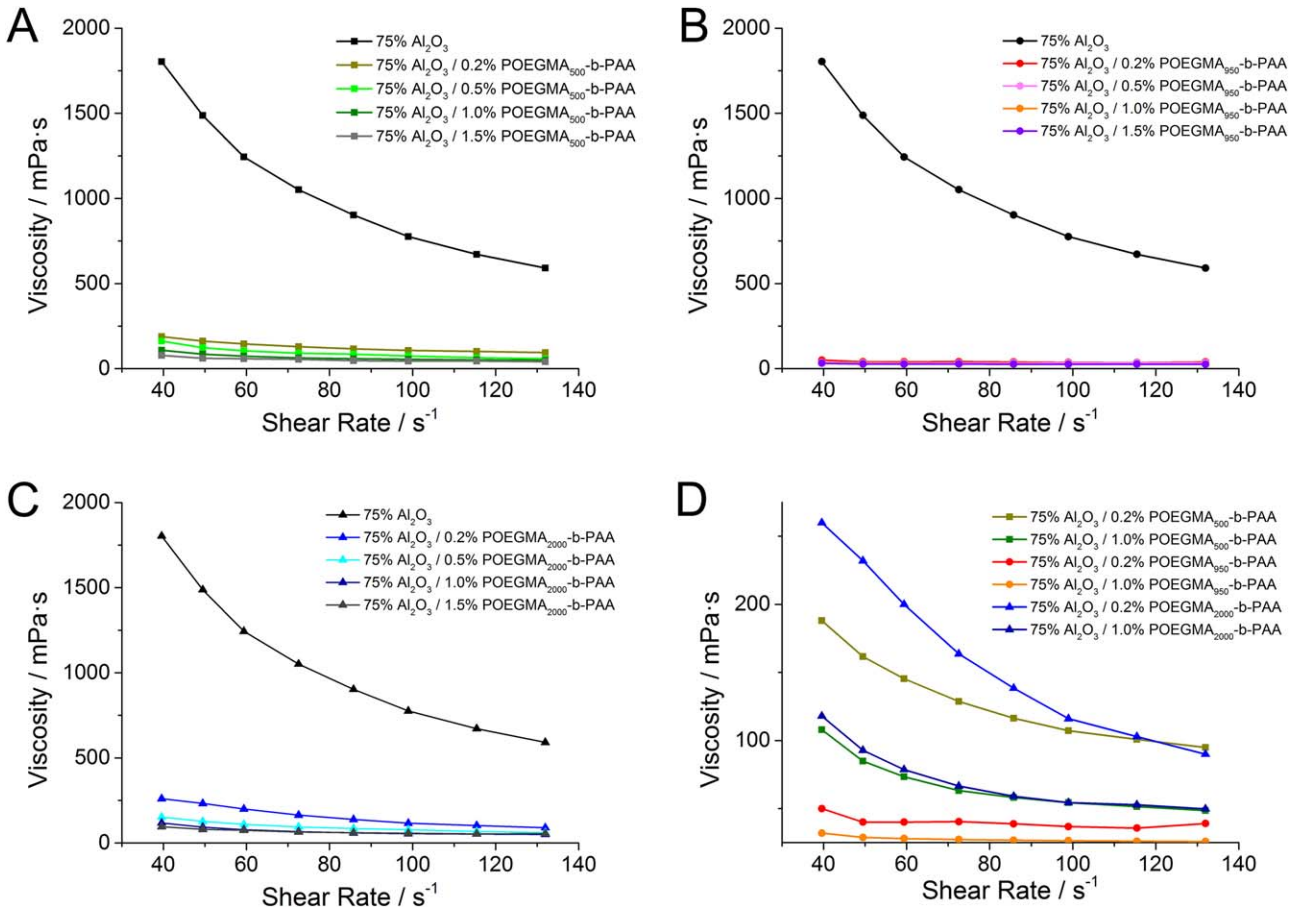

Figure 5. Apparent Viscosity curves versus shear rate of Al_2O_3 suspensions, with the addition of $POEGMA^{500}$-*b*-PAA (A), $POEGMA^{950}$-*b*-PAA (B), $POEGMA^{2000}$-*b*-PAA (C), and the comparison of different dispersants (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

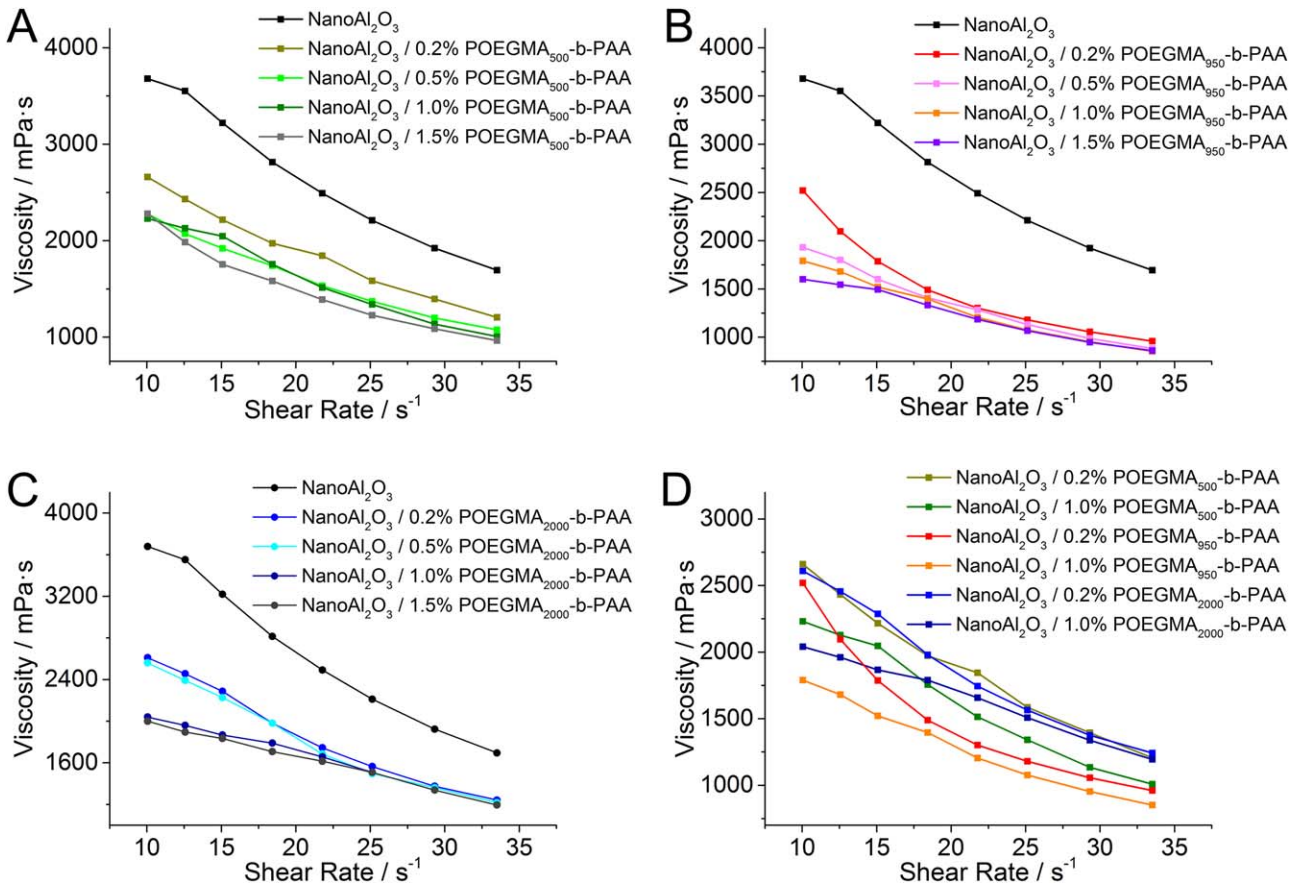

Figure 6. Apparent viscosity curves versus shear rate of Nano-Al_2O_3 suspensions, with the addition of $POEGMA^{500}$-*b*-PAA (A), $POEGMA^{950}$-*b*-PAA (B), $POEGMA^{2000}$-*b*-PAA (C), and the comparison of different dispersants (D). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Samples were taken at specific time intervals for kinetic researches. The reaction was terminated by immersing the reaction vessel in iced water after 10 h of polymerization. The obtained polymerization solution was dialyzed against deionized H_2O to remove salt, and the product POEGMA comb-CPA was isolated by lyophilization. The products were characterized by GPC, ^{1}H-NMR (solutions in D_2O), and FT-IR spectrum.

Synthesis of POEGMA-*b*-PAA. To a three-necked flask equipped with a magnetic stir bar were added POEGMA comb-CPA, AA, ACVA, and excess 0.01*M* $NaHCO_3$ aqueous solution as buffer. The solution was purged with nitrogen for 30 min and then heated to 70°C under stirring in a thermostated oil bath. The reaction was terminated and the product was isolated as same as that of POEGMA comb-CPA.

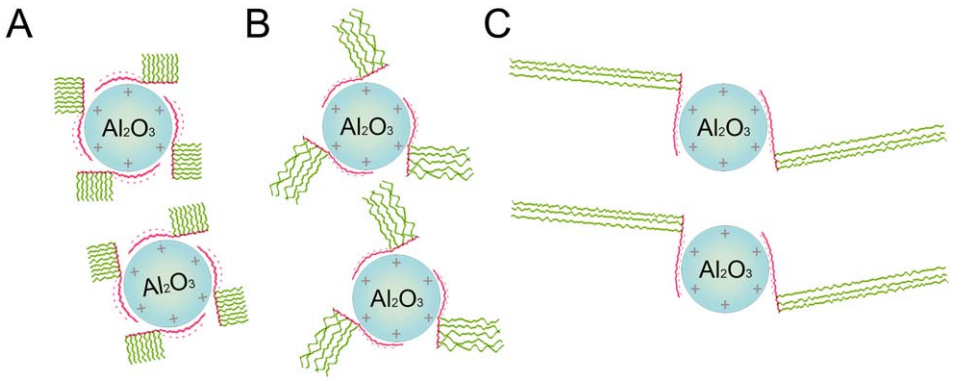

Figure 7. Dispersion mechanism diagram of comb polymer with different length of side chain (A) $PEOGMA^{500}$-*b*-PAA, (B) $PEOGMA^{950}$-*b*-PAA, (C) $PEOGMA^{2000}$-*b*-PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

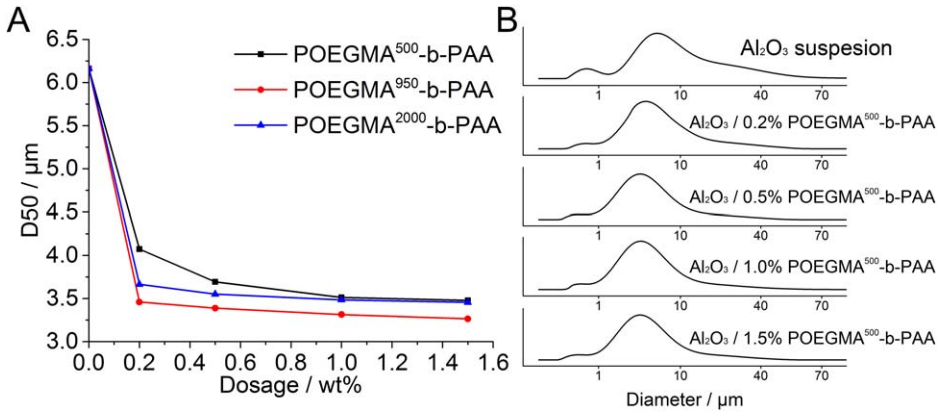

Figure 8. (A) Median diameter D50 of Al_2O_3 particles in suspensions with different amount of dispersants. (B) Granularity distribution curves of Al_2O_3 particles in suspensions with a series dosages of POEGMA^{500}-*b*-PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization and Methods

Spectrum Measurement. Fourier transform-infrared (FT-IR) spectrum was measured from KBr pellets of the samples on a NOCOLET NEXUS870 FT-IR spectrometer. Samples was dissolved in methanol, dropped onto KBr pellets and dried under an infrared lamp. ^{1}H-NMR was recorded using a Bruker Ultrashield 300 MHz NMR, employing D_2O as a solvent. Adsorption behavior of Al_2O_3 suspensions was tested using FT-IR spectrum. Samples consisted of 5 wt Al_2O_3 powders/95 wt water. POEGMA-*b*-PAA was added equal to 2% wt of Al_2O_3 powders in the suspension. Sample was dispersed under ultrasonic for 10 min and stirred overnight before centrifugation. The precipitation was washed for two more times by excess water and then dried under an infrared lamp.

Chromatograph Measurement. Size exclusion chromatography (SEC) measurements were carried out in 0.1 mol/L $NaNO_3$ aqueous solution at a flow rate of 1 mL/min using an Agilent 1260 HPLC with a set of different columns (Shodex SB806,806,803).

Zeta Potential Measurements. Zeta potential tests were measured on a Malvern Zetasizer Nano-ZS system at a constant temperature of 20°C. Zeta potential of Al_2O_3 suspensions was tested using NaOH solution (pH = 9.4–9.6) as background solvent. Samples consisted of 0.1 wt Al_2O_3 powders/100 wt solvent or 0.03 wt Nano-Al_2O_3 powders/100 wt solvent. POEGMA-*b*-PAA dispersant was added equal to 0.2 to 3% wt of Al_2O_3 powders in the suspensions.

Apparent Viscosity Measurements. Apparent viscosity was recorded using a Brookfield DV-2T rotation viscometer at a constant temperature of 20°C. Apparent viscosity of Al_2O_3 suspensions was tested using NaOH solution (pH = 9.4–9.6) as background solvent. Samples consisted of 75 wt Al_2O_3 powders/25 wt solvent or 30 wt Nano-Al_2O_3 powders/70 wt solvent. POEGMA-*b*-PAA dispersant was added equal to 0.5 to 3% wt of Al_2O_3 powders in the suspensions.

Granularity Measurements. Granularity test was measured on a Malvern Mastersizer 2000 system at a constant temperature of 20°C. Granularity of Al_2O_3 in the suspensions was tested using NaOH solution (pH = 9.4–9.6) as background solvent. Samples consisted of 0.08 wt Al_2O_3 powders/100 wt solvent or 0.05 wt Nano-Al_2O_3 powders/100 wt solvent. POEGMA-*b*-PAA dispersant was added equal to 0.2 to 1.5% wt of Al_2O_3 powders in the suspensions.

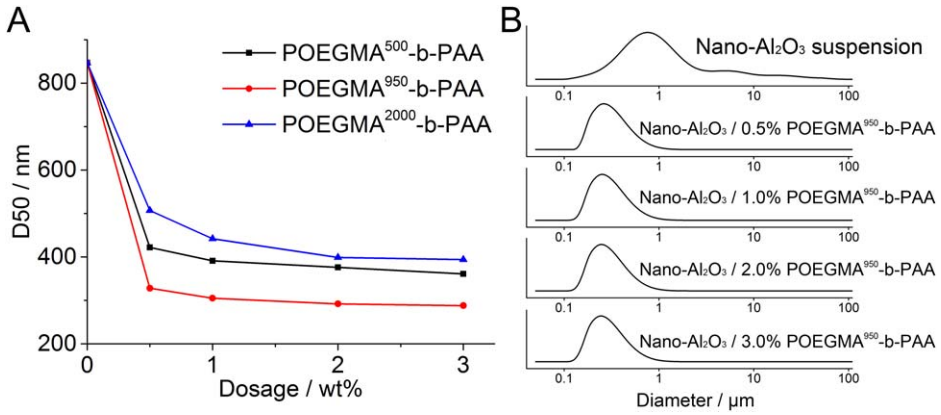

Figure 9. (A) Median diameter D50 of Nano-Al_2O_3 particles in suspensions with different amount of dispersants. (B) Granularity distribution curves of nano-Al_2O_3 particles in suspensions with a series dosages of POEGMA^{950}-*b*-PAA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

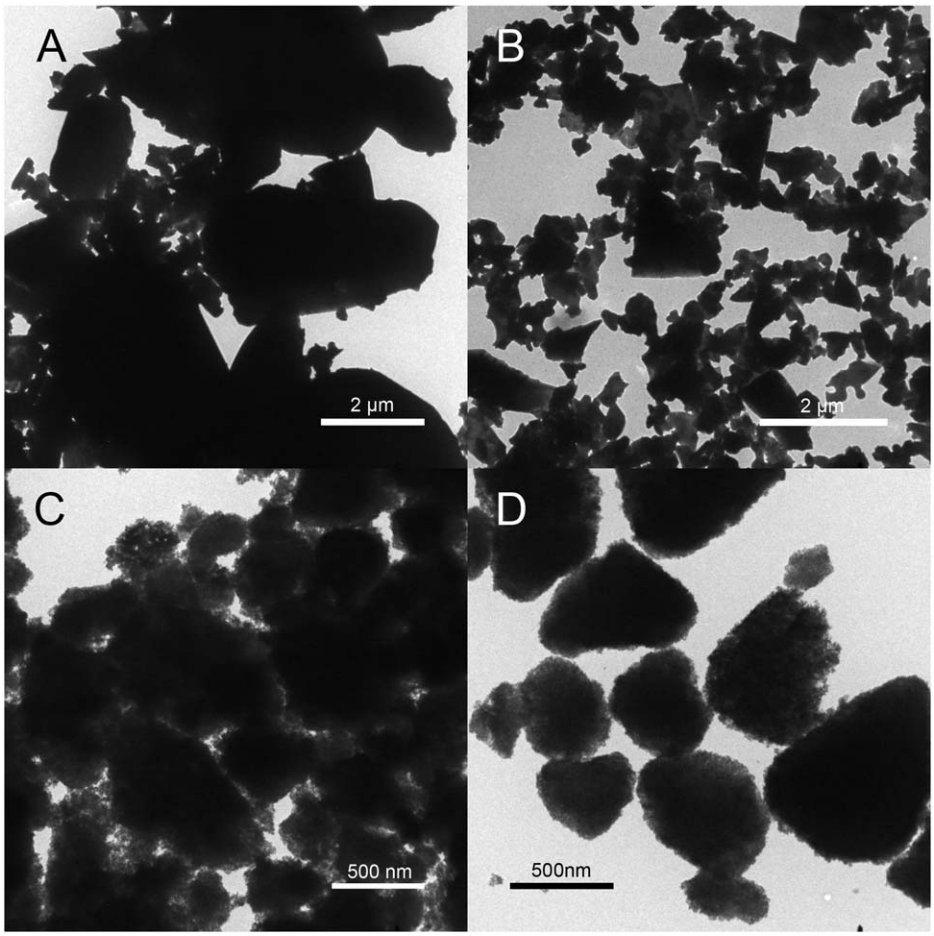

Figure 10. TEM images of Al_2O_3 (A), Al_2O_3/POEGMA^{950}-*b*-PAA (B), nano-Al_2O_3 (C), and nano-Al_2O_3/POEGMA^{950}-*b*-PAA (D).

Transmission Electron Microscopy (TEM). TEM images was photographed using a JEM 2100 High-Resolution Instrument. Al_2O_3 suspension was prepared using NaOH solution (pH = 9.4–9.6) as background solvent. Samples consisted of 0.2 wt Al_2O_3 powders/100 wt solvent or 0.12 wt Al_2O_3 powders/100 wt solvent. POEGMA-*b*-PAA dispersant was added equal to 0.5% wt of Al_2O_3 powders in the suspensions. Samples were dispersed under ultrasonic for 10 min and stirred overnight before dropping onto copper grids, and then dried under an infrared lamp before taking TEM images.

RESULT AND DISCUSSION

Synthesis of Comb Copolymer POEGMA-*b*-PAA

FT-IR spectra of OEGMA^{950}, POEGMA^{950} comb-CPA, and POEGMA^{950}-*b*-PAA is given in Figure 2. ^{1}H-NMR spectra of POEGMA^{950} comb-CPA and POEGMA^{950}-*b*-PAA is given in Supporting Information Figure S1. As seen in Figure 2, the main peaks are assigned to C-H stretching (2867 cm^{-1}), C═O stretching (1732 cm^{-1}), -CH_2- binding (1457 cm^{-1} and 1349 cm^{-1}), C-O stretching (1115 cm^{-1}),C-H binding of –OCH_3 (943 cm^{-1}) and C-O-C stretching (846 cm^{-1}). In Figure 2(C), we can find a board adsorption at wavenumber $\tilde{\nu} > 3000$ cm^{-1}, which corresponding to O-H vibration, as well as the peak at 1732 cm^{-1} strengthen. At the same time, comparing Supporting Information Figure S1(A,B), a tiny difference can be found around $\delta = 2.4$, which leads to the existence of PAA. These evidences indicate the existence of PAA block. We choose several different products to study in their dispersibility, as listed in Table.S1. They have similar PAA percentage, but their side chain lengths are different.

Absorption Behavior

FT-IR spectrum of Al_2O_3 and Al_2O_3/POEGMA-*b*-PAA reflects the constituent of Al_2O_3 particles before and after absorption. As shown in Figure 3, we can see several obvious differences between Figure 3(A,B), which leads to accumulation of some molecules with Al_2O_3 particles. Take the FT-IR spectrum of POEGMA-*b*-PAA into consideration, we infer that the POEGMA-*b*-PAA is absorbed onto the surface of Al_2O_3 particles. The anionic PAA chain of POEGMA-*b*-PAA was absorbed onto the positive-charged surface of Al_2O_3 particles by electrostatic attraction.

Analysis of Zeta Potential

Zeta potential reflects the variation of Al_2O_3 surface charge caused by the addition of POEGMA-*b*-PAA comb copolymer. POEGMA-*b*-PAA polymer plays the role of dispersant in the suspensions. Figure 4 shows the zeta potential of Al_2O_3 suspensions relative to the amount of dispersant added. In pace with the addition of POEGMA-*b*-PAA, the zeta potential of Al_2O_3 suspensions progressively decreases, owing to the absorption of

POEGMA-*b*-PAA on the surface of Al_2O_3 particles. Thus, with the increasing amount of dispersant, the absorption quantity increases and the zeta potential of Al_2O_3 suspensions becomes more negative, and finally reaches to a saturated value.

Analysis of Apparent Viscosity

Apparent viscosity reflects the aggregation of particles in the suspension. The apparent viscosity of Al_2O_3 and Al_2O_3/POEGMA-*b*-PAA suspensions are shown in Figures 5 and 6. Apparent viscosity decreases along with the increase of shear rate. With the adjunction of POEGMA-*b*-PAA, the viscosity of the suspensions evidently decrease. The suspensions perform as Newtonian fluid. Comparing the apparent viscosity curves of adding different dispersants in Figures 5(D) and 6(D), it is apparent that $POEGMA^{950}$-*b*-PAA has the best dispersibility. Take the data of Zeta potential into consideration, we can find out that the electrostatic repulsion is not the leading factor in dispersion, but the steric hindrance, which was described in former journals.[31–33] As shown in Figure 7, polymer with a shorter side chain may be absorbed more on the particle, but its steric hindrance is weaker. On the contrary, polymer with a longer side chain has stronger steric hindrance, but there may be less molecules absorbed on the particle. So, the polymer with an appropriate length of side chain has the best dispersibility. In such condition, the number of polymer molecules absorbed is large enough and the steric hindrance is relatively strong, as shown in Figure 7(B).

Analysis of Granularity

Granularity reflects the diameters and agglomeration of particles in the suspension. Granularity tests of Al_2O_3 and Al_2O_3/POEGMA-*b*-PAA suspensions are carried out and the results are shown in Figures 8 and [9]. It is found that the median diameter D50 of Al_2O_3 particles in suspensions distinctly reduce with the augment of polymer dispersants, as shown in Figures 8(A) and 9(A). At the same time, from Figures 8(B) and 9(B), we can find that the distribution of particle size is narrowed. Large-diameter particles almost disappear after adding enough dispersant, which means POEGMA-*b*-PAA polymers can scatter the agglomerated Al_2O_3 particles and improve the rheological properties of Al_2O_3 suspension. Similar with the results in viscosity measurement, $POEGMA^{950}$-*b*-PAA shows a better dispersibility than $POEGMA^{500}$-*b*-PAA and $POEGMA^{2000}$-*b*-PAA.

TEM Images

TEM images visually and intuitively show the dispersion of the Al_2O_3 particles in suspensions, as shown in Figure 10. Shown in Figure 10(A,C), without dispersant included, Al_2O_3/Nano-Al_2O_3 particles in suspensions agglomerate in quantity, which leads to the poor rheological properties of the suspensions. However, POEGMA-*b*-PAA plays a great role in preventing the aggregation of Al_2O_3 particles, which leads to the improvement of rheological properties of the suspensions.

CONCLUSIONS

Comb-like POEGMA-*b*-PAA, which can be synthesized using RAFT polymerization, is employed as the dispersant for Al_2O_3 suspensions for the first time. POEGMA-*b*-PAA polymers consist of an anionic PAA chain and a comb-like POEGMA chain. Two parts play different roles in dispersing Al_2O_3 suspensions. The PAA chain adsorb onto the surface of Al_2O_3 particles, while the POEGMA chain extend to the solution as well as provide enough steric hindrance to keep the suspension stable. The surface charge of Al_2O_3 particles changes from positive to negative after the addition of POEGMA-*b*-PAA. The rheological properties of Al_2O_3 suspensions, including apparent viscosity, medium diameter, or agglomeration, are also improved with the help of POEGMA-*b*-PAA. We find that the comb-like polymer with an appropriately modest length of side chain ($POEGMA^{950}$-*b*-PAA) provides the best dispersibility for the Al_2O_3 suspensions.

ACKNOWLEDGMENTS

This study is financially supported by National Natural Science Foundation of China (Nos. 51272100 and 51273073) and the Program of Changjiang Scholars and Innovative Research Team in University.

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