Synthesis of Poly(dodecyl methacrylate)s and Their Drag-Reducing Properties

Yuxin Ma,[1] Xilai Zheng,[1] Fengmei Shi,[2] Yue Li,[2] Shoujia Sun[3]

[1]*Environmental Engineering Department, Ocean University of Qingdao, Qingdao 266003, Shandong, China*
[2]*Environmental Science & Engineering Department, Qingdao University, Qingdao 266071, Shandong, China*
[3]*Environmental Engineering Department, Harbin Institute of Technology, Harbin 150001, Heilongjiang, China*

ABSTRACT: Dodecyl methacrylate was synthesized as the intermediate monomer for the preparation of poly(dodecyl methacrylate)s, which were synthesized with emulsion polymerization techniques. The intrinsic viscosities were measured, and the viscosity-average molecular weights were calculated. Polymers of dodecyl methacrylate with ultrahigh molecular weights (viscosity-average molecular weight $> 10^7$) were synthesized through orthogonal experiments. The drag-reduction properties of these polymers were studied in kerosene. The drag-reducing behavior of these polymers exhibited a strong dependence on the molecular weight and Reynolds number, and these polymers could be used as effective oil-soluble drag reducers and had good shear stabilities. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1622–1626, 2003

Key words: emulsion polymerization; infrared spectroscopy

INTRODUCTION

In the process of transferring a Newtonian fluid through a conduit, considerable energy may be expended to overcome friction encountered in the movement of the liquid. When a liquid is pumped under pressure, friction pressure is apparent as a pressure drop along the conduit, and such pressure drops are particularly noticeable under the condition of turbulent flow. To compensate for the loss of energy due to friction pressure, additional energy must be consumed. The use of drag reducers in a fluid lowers the energy consumption and increases the flow rate under the original pumping conditions. When they are added in small quantities (usually a few parts per million) to oil pipelines, they reduce the friction coefficient of turbulent flow. It is economically profitable for industrial organizations engaged in the movement of great amounts of liquids at high flow rates for considerable distances.

Most of the initial studies reported in the literature were focused on drag reducers in an aqueous environment.[1–3] The commercial application of oil-soluble drag reducers began in 1979 with the transport of crude oil in the trans-Alaska pipeline and attracted more attention.[4] There are many kinds of oil-soluble drag reducers, and they have different features. Polymers based on α-olefins have been used extensively as drag reducers,[5–12] but they have poor shear stability in the applications of such polymers.[13] Although surfactants can also be used as drag-reducing additives,[14,15] they are not in commercial applications so far. Several homopolymers and copolymers based on alkylstyrenes, alkylacrylates, and methacrylates are also known to be effective drag reducers. The polymers of dodecyl methacrylate with ultrahigh molecular weights [viscosity-average molecular weight (M_η) $> 10^7$] can also be used as effective oil-soluble drag reducers.[16] The extent of drag reduction increases as the molecular weight of the polymeric additive increases.[17,18] For enhanced shear stabilities, polymers associated by electrostatic, hydrogen-bonding, or hydrophobic interactions were synthesized,[19–21] but their poor solubility in oil restricted their use.

In this study, we synthesized the dodecyl methacrylate monomer and polymers with ultrahigh molecular weights ($M_\eta > 10^7$) and examined their IR spectroscopy. The maximum M_η value of the polymers synthesized was 1.75×10^7 (the maximum M_η value reported in the literature was 1.40×10^7, and the drag reduction was 68%[16]). These ultrahigh molecular weight polymers ($M_\eta > 10^7$) showed excellent drag-reduction properties and good shear stabilities.
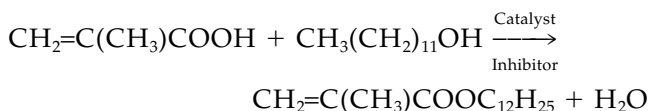
EXPERIMENTAL

Synthesis of the dodecyl methacrylate monomer

The monomer of dodecyl methacrylate was prepared by direct esterification with excess methacrylate and

dodecyl alcohol in the presence of both an esterifying catalyst and a polymer inhibitor:[22,23]

$$CH_2=C(CH_3)COOH + CH_3(CH_2)_{11}OH \xrightarrow[\text{Inhibitor}]{\text{Catalyst}}$$

$$CH_2=C(CH_3)COOC_{12}H_{25} + H_2O$$

Methacrylate (25.8 g), dodecyl alcohol (46.5 g), 4-methyl benzene sulfate (0.875 g), and hydroquinone (0.028 g) were taken in a 250-mL, three-necked flask. One neck was fitted with a condenser mounted on a water bath and linked with a vacuum device. Another neck was equipped with a thermometer. The flask was mounted in an atoleine bath. The reaction temperature was maintained at 105–115°C and under a certain level of vacuum for 4–5 h. The reaction gave a 99.2% conversion of dodecyl alcohol and excess methacrylate that could be 95.2% recovered. The residual products were washed with 10 mL of a 10% NaOH solution, washed with distilled water two or three times until they were colorless, and then distilled under a certain level of vacuum and at a certain temperature for the removal of the water. The product was used in the polymerization process.

Polymerization of dodecyl methacrylate

Triple-distilled water was weighed into a three-necked flask fitted with a thermometer, a nitrogen inlet, a nitrogen outlet, and a stirrer. The flask was mounted in a water bath maintained at certain temperature. The flask was flushed with nitrogen for 30 min and then was charged with an emulsifier (sodium dodecyl benzene sulfate and Triton-100), a polymerization initiator (potassium persulfate and sodium *meta*-bisulfite), and freshly distilled monomer. The polymerizations were carried out under a nitrogen atmosphere for several hours. The polymers from their emulsions were isolated through precipitation in cold methanol. The isolated polymers were dried *in vacuo* at 50°C.
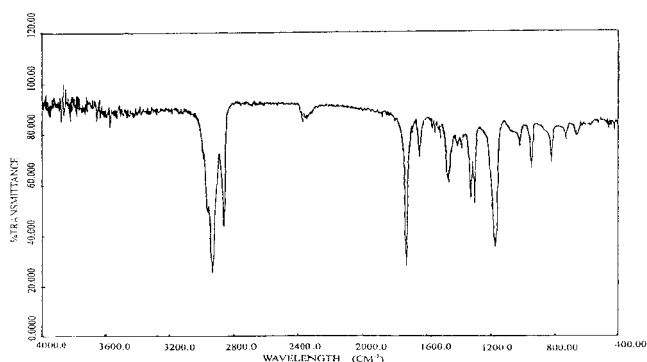
TABLE I
Comparative Absorption Frequencies in the IR Spectra of the Monomer and Polymers

Nature of the vibrations (functional groups in parentheses)	Wavelength positions of maxima (cm^{-1})	
	Monomer	Polymers
C–H str. vib. (C=CH$_2$)	2995	—
C–H str. vib. (–CH$_2$–)	2924	2924
	2854	2854
C=O str. vib. (ester)	1742	1742
C=C str. vib. (alkene)	1643	—
C–H def. vib. (–CH$_2$–)	1456	1456
C–H def. vib. (C–CH$_3$)	1320	1320
C–H I.P. def. vib. (C=CH$_2$)	1245	1245
	1250	1250
C=O str. vib. (ester)	1200	1200
C–H O.O.P. def. vib. (C=CH$_2$)	950	—
C–H O.O.P. def. vib. (CH–CH$_2$)	860	860
C–H str. vib. (=CH$_2$)	720	—

str. = stretching; I.P. = in plane; O.O.P. = out of plane; vib. = vibrations.

M_η determination

Approximate M_η values were calculated with the well-known Mark–Houwink–Sakurada equation. The measurements of the solution viscosity were made at a constant temperature with Cannon-Ubbelohde semi-micro dilution viscometers. The solvent efflux times were kept longer than 80 s by means of the proper selection of the viscometer size. It was assumed that the effect of the shear rate would be minimal for efflux times of this magnitude; consequently, no shear corrections were applied to the data. Intrinsic viscosities ($[\eta]$) were determined with the standard procedure of extrapolating viscosity numbers to infinite dilution. Chinai and Guzzi[24] determined the relationship between $[\eta]$ and M_η for poly(dodecyl methacrylate) in butyl acetate at 23°C: $[\eta] = 0.864 \times 10^{-5} M_\eta^{0.64}$. The temperatures for the measurements were controlled within ±0.05°C.

Drag-reduction-property determination

Drag-reduction studies were carried out in a capillary flow apparatus with kerosene as a carrier fluid. The
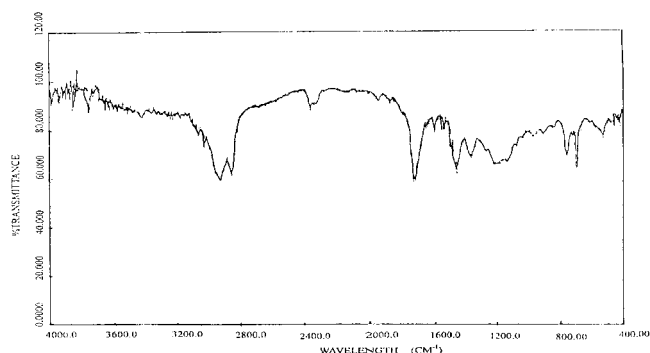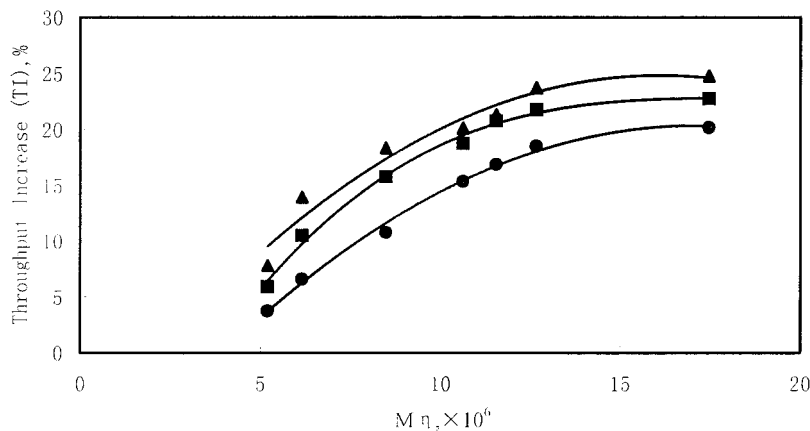

Figure 1 IR spectrum of the dodecyl methacrylate monomer.

Figure 2 IR spectrum of the dodecyl methacrylate polymers.

Figure 3 Variation of the TI percentage with the polymer molecular weight at various concentrations: (●) 0.01, (■) 0.02, and (▲) 0.03 wt %.

apparatus was a cylindrical, jacketed vessel fitted with a pressure gauge, an addition funnel, an air inlet, and an outlet with a 100-cm-long capillary tube and a 2.0-mm inside diameter. The fluid for testing could be pressurized up to 0.4 MPa by means of a compressed gas.

The drag reduction was evaluated in terms of the throughput increase (TI) by the measurement of the volumetric flow rate of kerosene and that of the polymer solution in kerosene at a given pressure. The TI percentage was calculated with the following equation:

$$M\eta = 1.27 \times 10^7 \, (\bullet); \quad M\eta = 6.16 \times 10^6 \, (\blacksquare)$$

where Q_1 and Q_2 are the volumetric flow rates of kerosene and the polymer solution in kerosene, respectively.

Shear-stability determination

The polymer solutions were characterized for their shear stability by the determination of the ratio of TI at a particular pass number to the initial throughput increase (TI_0) at a wall-shear rate of around 9000 s^{-1}. The solutions were rested for about 15 min after each pass.

IR spectroscopy of the monomer and polymers

A typical IR spectrum of the dodecyl methacrylate monomer is shown in Figure 1. The correlations between the absorption maxima related to the functional groups and frequencies are shown in Table I. The IR spectra of the dodecyl methacrylate polymers were taken in petroleum ether. A typical IR spectrum of the dodecyl methacrylate polymers is shown in Figure 2. The correlations between the absorption maxima related to the functional groups and frequencies are shown in Table I.

RESULTS AND DISCUSSION

The extent of drag reduction increases as the molecular weight of the polymeric additive increases. For
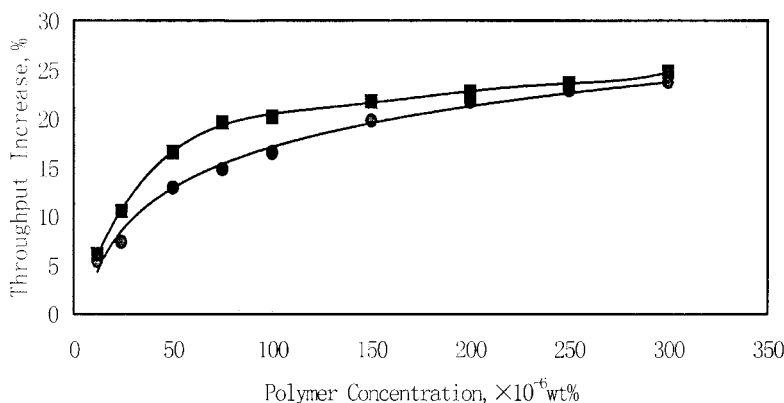
Figure 4 Variation of the TI percentage with the polymer concentration for polymers with different values of M_η: (●) 1.27 × 10^7 and (■) 1.75 × 10^7.
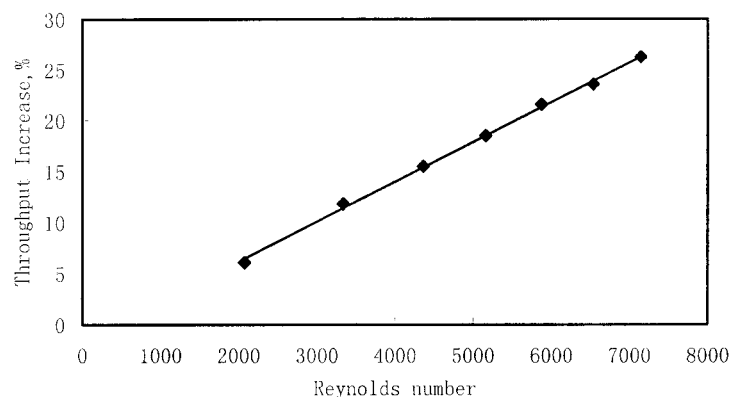
Figure 5 Variation of the TI percentage with the Reynolds number.

good drag-reduction properties when poly(dodecyl methacrylate)s are added to kerosene solutions, the molecular weights of these polymers should be increased. Many attempts and orthogonal experiments have been made to optimize the reaction conditions to obtain polymers with ultrahigh molecular weights. The reaction time and the concentration of the emulsifier are key factors that influence the molecular weights, and increasing the dose of the emulsifier may not only increase the rate of the polymerization reaction but also increase the M_η values of the polymers. A series of polymers with various molecular weights were synthesized by various polymerization reaction conditions, and their drag-reduction properties in kerosene were studied. The maximum M_η value of the polymers synthesized was 1.75×10^7. The conditions of this experiment were as follows: 100 mL of distilled water, 1.0 g of sodium dodecyl benzene sulfate, 1.0 mL of Triton-100, 2 mL of potassium persulfate (2.0%), and 2 mL of sodium meta bisulfate (1.0%), 11.3 g of the monomer, a reaction temperature of $55 \pm 2°C$, and a reaction time of 48 h (yield = 97–100%).

The TI values of the polymers were measured with the same Reynolds number (5850) and measuring temperature (20°C) at various concentrations (0.01, 0.02, and 0.03 wt %), as shown in Figure 3. An increased molecular weight enhanced the drag-reduction properties. Figure 4 shows data for these polymers (M_η

= 1.27×10^7 or 1.75×10^7) at various concentrations with the same Reynolds number (5850) and measuring temperature (20°C): the highest concentration gave the highest drag-reduction percentage. It is possible that the ideal drag reduction could have been obtained for these polymer samples at a concentration of more than 0.01 wt %. When the concentration exceeded 0.01 wt %, the polymer solution showed little concentration dependence. Figures 3 and 4 also show that the polymers with higher molecular weights had higher TI values even at lower concentrations. At higher concentrations, TI only went up a little with the increase in the concentrations. Polymers with lower molecular weights could not achieve higher TI values unless they were added in higher concentrations.

The variation of the drag reduction with the Reynolds number ($M_\eta = 1.16 \times 10^7$) is shown in Figure 5. With the Reynolds number increasing, there was an increase in the extent of drag reduction.

The degradation of long-chain molecules occurs under turbulent flow because of the high shear stresses present in such fields. The shear stabilities of the polymers ($M_\eta = 1.27 \times 10^7$ or 6.16×10^6) are shown in Figure 6. They were measured at a concentration of 0.03 wt % and at a shear rate of 9000 s^{-1}. The polymer with the higher molecular weight had good shear stability and retained about 85% of its initial value of TI (cf. 80% for the polymer with the lower molecular
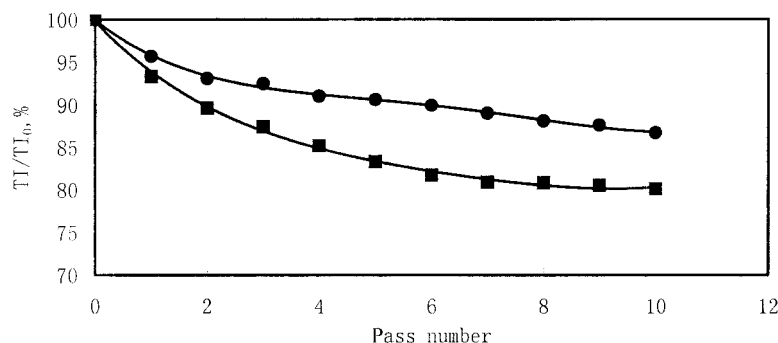

Figure 6 Shear stability of the polymers at a shear rate of 9000 s^{-1}: ($\bullet$) $M_\eta = 1.27 \times 10^7$ and ($\blacksquare$) $M_\eta = 6.16 \times 10^6$.

weight) after 10 passes at a wall-shear rate of approximately 9000 s^{-1}.

References

1. Ram, A.; Finkelstein, E.; Elata, C. Ind Eng Chem Process Res 1967, 6, 309.
2. Savins, J. G. J Soc Pet Eng 1964, 4, 203.
3. Astarita, G. Ind Eng Chem Fundam 1965, 4, 354.
4. Burger, E. D.; et al. J Pet Technol 1982, 34, 377.
5. Burger, E. D.; Chorn, L. G.; Perkins, T. K. J Rheol 1980, 24, 603.
6. U.S. Pat. 3,827,447 (1974).
7. U.S. Pat. 3,357,402 (1974).
8. U.S. Pat. 3,559,664 (1971).
9. U.S. Pat. 3,692,676 (1972).
10. U.S. Pat. 3,801,508 (1974).
11. U.S. Pat. 3,215,154 (1965).
12. Hershey, H. G.; Zakin, J. L. Chem Eng Sci 1967, 22, 1847.
13. Ram, A.; Kadim, A. J Appl Polym Sci 1970, 14, 2145.
14. Bewersdorf, H. W.; Ohlendorf, D. Colloid Polym Sci 1988, 266, 1.
15. Zakin, J. L. Nat Phys Sci 1971, 235, 97.
16. Holtmyer, M. D.; Chatterji, J. Polym Eng Sci 1980, 20, 473.
17. Zakin, J. L.; Huston, D. L. J Macromol Sci Phys 1980, 18, 795.
18. Brostow, W. Polymer 1983, 24, 63.
19. U.S. Pat. 5,080,121 (1992).
20. Malik, S.; Shintre, S. N.; Mashelkar, R. A. Macromolecules 1993, 26, 55.
21. Malik, S.; Mashelkar, R. A. Chem Eng Sci 1995, 50, 117.
22. Jpn. Pat. 61176555 (1985).
23. Ma, Y. X.; Sun, S. J. J Qingdao Uni (Eng) 1999, 14(2), 62.
24. Chinai, S. N.; Guzzi, H. A. J Polym Sci 1958, 41, 475.