Synthesis of Methacrylate Copolymers and Their Effects as Pour Point Depressants for Lubricant Oil

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ABSTRACT: In this study, polymethacrylate polymers were synthesized by free-radical polymerization for use as pour point depressants in lubricant oil, and their low-temperature properties were investigated. Four methacrylate monomers were synthesized by the esterification of methyl methacrylate (MMA) with four kinds of fatty alcohols. The purification step was performed to prepare the pure monomers. Two polymerization experiments were carried out with four kinds of methacrylate monomers obtained previously and MMA. Copolymers, which were made from one kind of monomer and MMA, and terpolymers, which were made from two kinds of monomers and MMA, were prepared. The molecular structures of the synthesized methacrylate monomers and polymethacrylate polymers were verified by ^{1}H-NMR, and the molecular weight data were obtained by gel permeation chromatography. The pour points of the base oils containing 0.1 wt % polymethacrylate polymers were measured according to ASTM D 97-93. The pour points of most base oils containing each polymer decreased compared to that of the pure base oil. Particularly, poly(dodecyl methacrylate-*co*-hexadecyl methacrylate-*co*-methyl methacrylate), made of dodecyl methacrylate, hexadecyl methacrylate, and MMA at a molar ratio of 3.5 : 3.5 : 3, showed the best low-temperature properties. This terpolymer dropped the pour point of the base oil by as much as 23°C, and its yield was 93.5%. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2579–2586, 2011

Key words: additives; copolymerization; esterification

INTRODUCTION

A lubricant is a substance that is used between two surfaces of moving materials to reduce the friction generated between them. There are many types of lubricants, including gases, liquids, solids, and grease.[1] Among them, liquid lubricants are most often used. Liquid lubricants are mixtures that consist of about 90% base fluids and less than 10% chemical additives. The base fluids act as a lubricant primarily by separating the fluid layer from the moving surfaces and should easily remove any generated heat. The base oil, usually referred to as mineral oil, meets these requirements; thus, it is typically used as the base fluid. The lubricant oil is the mixture of the base oil and some chemical additives, which have specific properties and abilities. Many properties of the lubricants are determined or enhanced by the addition of various chemical additives to the base oil. For example, viscosity index improvers optimize the viscosity of the lubricants under high- and low-temperature conditions, oxidation inhibitors reduce the oxidation of the lubricants, and antiwear agents impart abrasion-proof properties to the lubricants.[2–4] Pour point depressants (PPDs) are also a kind of chemical additive that lower the pour point of the base oil so that the performance of the base oil at low temperatures can be improved.

The *pour point* is the lowest temperature at which the base oil cannot flow. The majority of crude oils contain a large amount of oil waxes called *paraffin.* The base oil also has substantial amounts of paraffin because it is produced in the refining process of crude oil. Paraffins are mixtures of hydrocarbons with linear chains that contain mainly 20–40 carbon atoms in addition to alkanes with branched and cyclic chains.[5] The solubility of the paraffins present in the base oil decreases with decreasing temperature. Consequently, the first crystal appears at a certain temperature, called the *cloud point* or *wax appearance temperature.*[6,7] As the temperature decreases below this point, paraffin crystals grow and form platelets, needles, and orthorhombic structures. They overlap and interlock with each other and, thereby, form three-dimensional networks. The oil remaining around this network gets trapped in it, and the gel-like structure is made.[8–11] This gel becomes sufficiently dense with further cooling, which causes the

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oil to solidify apparently. Upon further decreases in temperature, the complexity of the structure increases, and finally, the movement of the oil ceases at the pour point.[12]

Paraffin deposition is one of the most important problems with base oil, which consists mostly of paraffinic oil when it is applied under low-temperature conditions. The intensive dewaxing of oil during refining can reduce the pour point of the base oil. However, this procedure decreases the oxidation stability of the oil and increases its tendency to deposit carbon.[13] The addition of PPDs to the base oil is a reasonable solution to this problem. There are some characteristics of the additives that must be considered when they are being used to reduce the pour point: there must be a sufficient number of pendant alkyl groups with sufficiently long hydrocarbon chains, there must be an appropriate distance between the hydrocarbon pendant chains, and there must be a suitable ratio of monomers when a copolymer is used.[14–17]

In this study, polymethacrylate polymers were used as the PPDs of the base oil. Polymethacrylate polymers satisfy the characteristics required for a PPD to be efficient, as described previously. They are commonly used in a variety of applications because of their excellent low-temperature properties. In this study, many kinds of polymethacrylate polymers were synthesized, and their low-temperature properties were investigated. Four kinds of monomers were prepared by the synthesis of methyl methacrylate (MMA) and four different fatty alcohols, dodecanol, tetradecanol, hexadecanol, and octadecanol. The polymethacrylate polymers were polymerized with MMA and four kinds of synthesized monomers in various ratios. The polymethacrylate polymers were introduced into the base oil, and the pour point of the base oils was measured.

EXPERIMENTAL

Materials

Four kinds of fatty alcohols were selected as raw materials for the synthesis of the methacrylate monomers: 1-dodecanol, 1-tetradecanol, 1-hexadecanol, and 1-octadecanol. All alcohols were purchased from Aldrich (St. Louis, MO). MMA was used in the synthesis of the methacrylate monomers and polymethacrylate polymers and was purchased from Aldrich. Sulfuric acid and hydroquinone were also purchased from Aldrich and were used as the catalyst and inhibitor, respectively, in the synthesis of the methacrylate monomers. α,α'-Azobisisobutyronitrile (AIBN) was the initiator and was purchased from Junsei (Tokyo, Japan). The base oil was obtained from GS Caltex (Seoul, Korea), contained 68.02% paraffinic and 31.98% naphthenic oil, and had a Saybolt universal second of 150.

Synthesis of the methacrylate monomers

Alkyl methacrylates were prepared by the esterification of MMA with fatty alcohols in the presence of sulfuric acid as the catalyst and hydroquinone as the inhibitor. Dodecanol and MMA were added (1 : 2 molar ratio) in addition to sulfuric acid (0.5 mol %) and hydroquinone (3 wt % compared with MMA) in a round flask connected to a cooling condenser and fitted in a controlled heating mantle. These materials were heated to 90°C for 18 h with constant stirring to react with each other. Afterward, the unreacted MMA was removed from the product under reduced pressure through a gradual increase in the temperature until distillation was complete. The synthesized product was purified to remove the unreacted dodecanol and hydroquinone. We performed the purification process by pouring the product into an excess volume of methanol, which was about two times as much as the synthesized product, and separating the product from the methanol. The desired monomer, dodecyl methacrylate (DDMA), was obtained through this procedure. The other alcohols, tetradecanol, hexadecanol, and octadecanol, were reacted under the same experimental conditions. With this approach, tetradecyl methacrylate (TDMA), hexadecyl methacrylate (HDMA), and octadecyl methacrylate (ODMA) were obtained.

Polymerization of the polymethacrylate polymers

All of the polymers were prepared by free-radical polymerization of the synthesized monomers with MMA in toluene with AIBN as the initiator. Two types of polymethacrylate polymers were polymerized: one was made from one kind of monomer and MMA (copolymer), and the other was made from two monomers and MMA (terpolymer).

Polymerization of the copolymers

DDMA and MMA in toluene were added (at a 7 : 3 molar ratio) to a three-necked round flask equipped with a cooling condenser, controlled heating mantle, and inlet for nitrogen gas. AIBN (1 mol %) was used as the initiator. The reaction was carried out at 70°C for 4 h under constant stirring and a nitrogen atmosphere. After completion of the reaction, the toluene was distilled off under reduced pressure. The remaining product was purified in chloroform/methanol and vacuum-dried at 75°C until the weight was constant. Poly(dodecyl methacrylate-*co*-methyl methacrylate) (PDDMMA) was obtained through this procedure. The different kinds of PDDMMA were also obtained by the reaction of DDMA and MMA at 5 : 5 and 3 : 7 molar ratios. Poly(tetradecyl methacrylate-*co*-methyl methacrylate) (PTDMMA), poly(hexadecyl methacrylate-*co*-methyl methacrylate) (PHDMMA), and poly(octadecyl methacrylate-*co*-methyl methacrylate) (PODMMA) were prepared with TDMA, HDMA, and ODMA, respectively, instead of DDMA in the same manner.

Polymerization of the terpolymers

The other type of polymer was obtained with DDMA, TDMA, and MMA (at a 3.5 : 3.5 : 3 molar ratio). The experimental conditions were same as those used in the preparation of the copolymers, except for the monomer that was used in the reaction. The other five terpolymers were synthesized with two monomers and MMA in the same manner. Two monomers were selected from the four kinds of previously synthesized monomers.

Characterization

The structures of all reagents, the methacrylate monomers, and the polymethacrylate polymers synthesized previously were determined with ^{1}H-NMR spectroscopy data. The ^{1}H-NMR spectra of all of the products were obtained at 300 MHz on a Varian (Santa Clara, CA) Mercury 300 spectrometer with deuterated chloroform ($CDCl_3$) as the solvent. The average molecular weights were measured for the polymethacrylate polymers by gel permeation chromatography. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) were measured with a Waters 1515 system equipped with a refractive-index detector (Waters 2414) and Waters Styragel HR columns. The measurements were performed at room temperature with tetrahydrofuran as the mobile phase at a flow rate of 1.0 mL/min. Calibration parameters were obtained with a polystyrene standard. We obtained the polydispersity index (PDI) by dividing M_w by M_n. As the polymer chains became uniform, the value of the PDI approached 1.

Pour point measurement

The synthesized polymers were evaluated as PPDs with the base oil through pour point tests according to the ASTM D 97-93 standard method.[18] The polymers (0.1 wt % compared with the base oil) were added to the base oil, and the mixtures were heated at 60°C for 2 h to dissolve the polymers in the base oil. A Tanaka (Tokyo, Japan) pour point tester (model MPC-602) was used to measure the pour points of the prepared base oil mixtures. The prepared samples were maintained at 40°C for a given time and were then placed into testing vials. They were cooled in a cooling bath, and the temperature was dropped by 1°C up to the pour point. The target temperature was set to −45°C.

RESULTS AND DISCUSSION

Synthesis of the methacrylate monomers

The first synthesis of DDMA was carried out by the esterification of MMA with dodecanol, as described in the Experimental section. After synthesis for 18 h, a light yellow liquid, which was a mixture of DDMA, residual MMA, and hydroquinone, was obtained. The residual MMA, whose presence was caused by the use of a large amount of MMA for the complete reaction, was distilled off under reduced pressure through a gradual increase in the temperature until distillation was complete. The presence of MMA in the product hindered the purification of the monomer, so the complete removal of MMA was essential before the purification step. The purification of DDMA was performed with methanol to remove hydroquinone. Pure DDMA, which was a light yellow liquid, was obtained through several purification steps with an average yield of 79.44%. The other monomers, TDMA, HDMA, and ODMA, were obtained by the same procedure used to prepare the pure DDMA. Because the melting points of TDMA, HDMA, and ODMA were around room temperature, purification was more efficient when the molten product was used to remove the hydroquinone. After the removal of MMA and purification of the product, a yellow liquid of pure TDMA, a transparent liquid of pure HDMA, and a dark red liquid of pure ODMA were obtained. The average yields of TDMA, HDMA, and ODMA were 78.89, 82.57, and 82.93%, respectively.

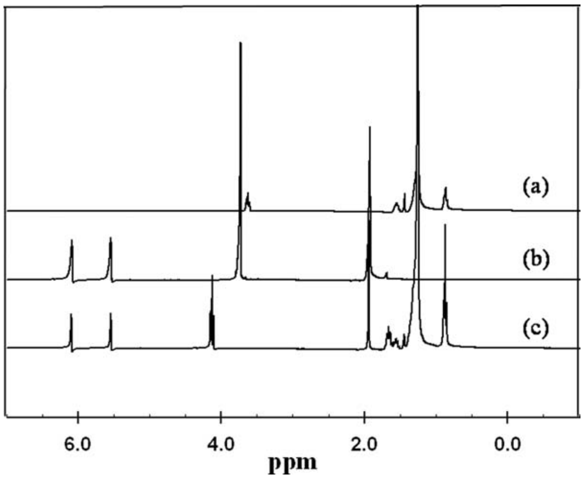

Figure 1 ^{1}H-NMR spectra of (a) dodecanol, (b) MMA, and (c) DDMA.

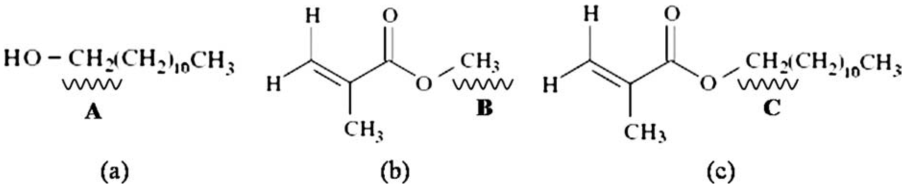

Figure 2 Molecular structures of (a) dodecanol, (b) MMA, and (c) DDMA.

The structures of the pure DDMA obtained through the previous procedure and its raw materials were confirmed by ^{1}H-NMR. Figure 1 shows the ^{1}H-NMR spectral changes of the DDMA before and after the esterification. There were some differences among the ^{1}H-NMR spectra. The peaks observed at 3.62 and 3.73 ppm in the ^{1}H-NMR spectra of dodecanol and MMA, respectively, were not present in the ^{1}H-NMR spectrum of DDMA, but instead, a peak at 4.13 ppm was observed in the ^{1}H-NMR spectrum of DDMA. The peak at 3.62 ppm was caused by protons in the $-CH_2$ group [A in Fig. 2(a)], and its shift to 4.13 ppm was caused by protons in the $-CH_2$ group [C in Fig. 2(c)]. In addition, the peak at 4.13 ppm was a triplet, which was also observed in the peak at 3.62 ppm but not in the peak at 3.73 ppm. These results showed that the reaction was carried out to completion. The ^{1}H-NMR spectra of TDMA, HDMA, and ODMA are shown in Figure 3. They were identical in the multiplicity of peaks and in the chemical shift, differing only in the intensity of the peaks caused by protons in the $-CH_2$ groups. Hence, TDMA, HDMA, and ODMA were also obtained after the completion of the reaction.

Polymerization of the polymethacrylate polymers

Polymerization of the copolymers

The first types of polymers were prepared with one of the methacrylate monomer synthesized previously and MMA. Among them, PDDMMA was polymerized first with DDMA and MMA at a 7 : 3 molar ratio. The copolymerization reaction was performed with AIBN as the initiator of the free-radical reaction in the toluene solvent. After copolymerization for 4 h, the highly viscous liquid dissolved in toluene. The toluene was removed under a reduced pressure, and the product was purified. Because the product was very viscous and solidified easily at room temperature, it was first dissolved in chloroform. Various purification steps were then performed to achieve a highly purified product. The final product of PDDMMA was obtained after drying, and its average yield was determined to be 92.9%. The other PDDMMA was polymerized at DDMA : MMA molar ratios of 5 : 5 and 3 : 7. As the amount of MMA increased, the product became more easily hardened and had a lower yield. The average yields of PDDMMA were 87.5 and 79.6% at 5 : 5 and 3 : 7 molar ratios of DDMA and MMA, respectively. The experimental procedure established in the polymerization of PDDMMA was used in the polymerization of PTDMMA, PHDMMA, and PODMMA, which were polymerized with MMA and TDMA, HDMA, and ODMA at molar ratios of 7 : 3, 5 : 5, and 3 : 7, respectively, of MMA and each methacrylate monomer. The average yields of each reaction are shown in Table I.

The ^{1}H-NMR spectra of the polymerized polymers were obtained, and the spectra of PODMMA : MMA at molar ratios of 7 : 3, 5 : 5, and 3 : 7 and each methacrylate monomer are shown in Figure 4. The spectra of the four polymethacrylate polymers made with methacrylate monomers and MMA at a molar ratio of 7 : 3 are presented in Figure 5. These spectra were very similar because there were only trivial differences in the number of hydrogen atoms in the side chains. As the amount of MMA increased, the intensity of the peak at 3.59 ppm increased; this indicated that the molar fraction of MMA in the PODMMA copolymers increased. The molecular weight data obtained from gel permeation chromatography are shown in Table I. M_n varied from 23,000 to 43,000, depending on the kind of methacrylate monomer used and the composition of the copolymers.

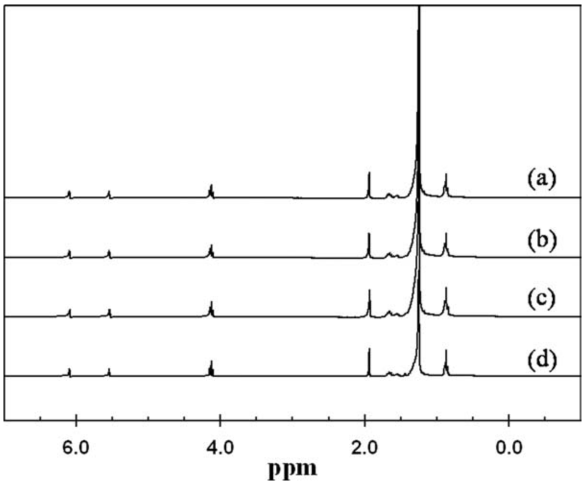

Figure 3 ^{1}H-NMR spectra of (a) DDMA, (b) TDMA, (c) HDMA, and (d) ODMA.

TABLE I
Molar Weight Data and the Average Yield of the Copolymers

Copolymer	Composition (alkyl methacrylate : MMA)	Molar weight M_w	Molar weight M_n	PDI (M_w/M_n)	Yield (%)
PDDMMA1	7 : 3	92,972	39,590	2.348	92.9
PDDMMA2	5 : 5	83,942	37,791	2.221	87.5
PDDMMA3	3 : 7	78,470	37,669	2.083	79.6
PTDMMA1	7 : 3	95,167	43,430	2.191	95.0
PTDMMA2	5 : 5	77,939	35,621	2.188	88.1
PTDMMA3	3 : 7	49,143	23,523	2.089	86.4
PHDMMA1	7 : 3	98,801	41,928	2.339	92.6
PHDMMA2	5 : 5	64,795	30,811	2.103	87.5
PHDMMA3	3 : 7	59,334	28,451	2.086	78.9
PODMMA1	7 : 3	106,446	47,921	2.221	95.5
PODMMA2	5 : 5	90,369	43,105	2.096	90.9
PODMMA3	3 : 7	48,811	23,956	2.038	84.5

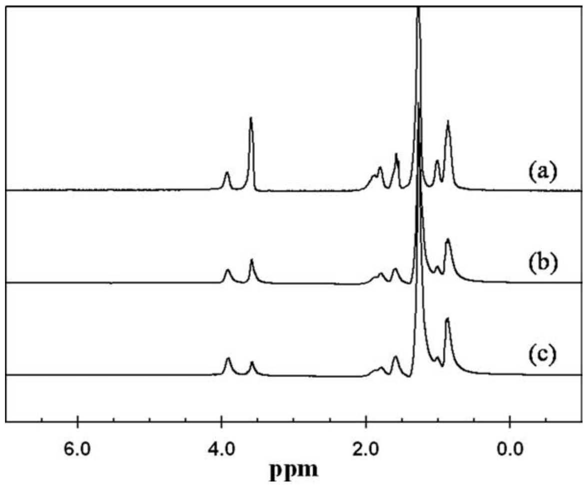

Figure 4 ^{1}H-NMR spectra of PDDMMA polymerized with DDMA and MMA at molar ratios of (a) 3 : 7, (b) 5 : 5, and (c) 7 : 3.

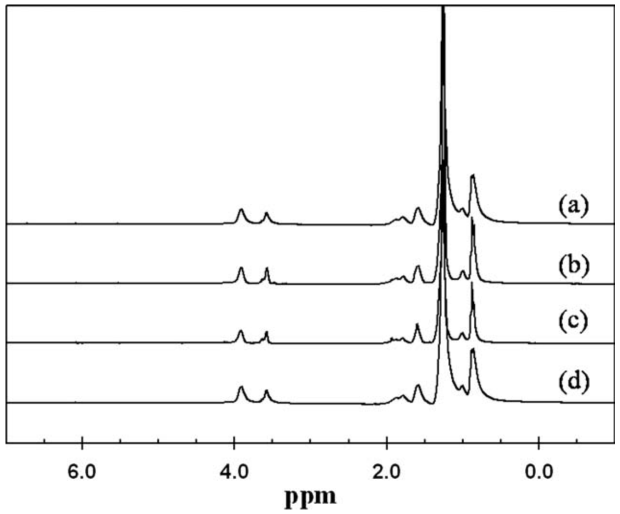

Figure 5 ^{1}H-NMR spectra of (a) PDDMMA, (b) PTDMMA, (c) PHDMMA, and (d) PODMMA.

Polymerization of terpolymers

The second type of polymer was polymerized with two kinds of methacrylate monomer and MMA. Six kinds of terpolymers were prepared by polymerization with each group and MMA with the same experimental procedures described previously. The groups were made in pairs among the four kinds of methacrylate monomers. The average yields of the terpolymers obtained through these procedures are listed in Table II; in general, the yields were above 93%. The ^{1}H-NMR spectrum of poly(dodecyl methacrylate-*co*-hexadecyl methacrylate-*co*-methyl methacrylate) (PDDHDMMA) is shown with the ^{1}H-NMR spectra of the PDDMMA and PHDMMA in

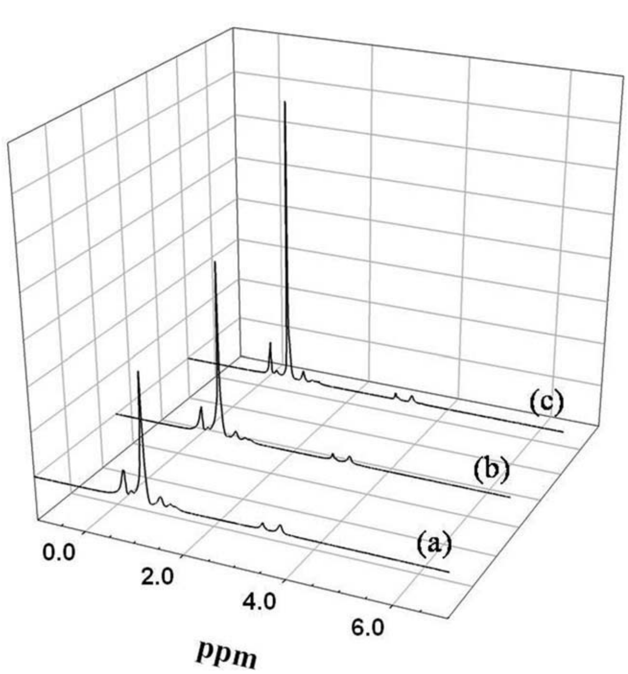

Figure 6 ^{1}H-NMR spectra of (a) PDDMMA, (b) PDDHDMMA, and (c) PHDMMA.

TABLE II
Molar Weight Data and the Average Yield of the Terpolymers

Terpolymer	Monomers	Molar weight M_w	Molar weight M_n	PDI (M_w/M_n)	Yield (%)
PDDTDMMA	DDMA/TDMA	75,275	31,846	2.364	93.1
PDDHDMMA	DDMA/HDMA	73,407	31,027	2.366	93.5
PDDODMMA	DDMA/ODMA	100,253	47,117	2.128	94.5
PTDHDMMA	TDMA/HDMA	85,497	37,960	2.252	94.2
PTDODMMA	TDMA/ODMA	76,617	37,473	2.045	95.1
PHDODMMA	HDMA/ODMA	107,831	49,193	2.192	94.5

TABLE III
Pour Points of the Base Oils Containing the Polymethacrylate Polymers

Polymethacrylate polymers	Pour point (°C; measured)	Descent in pour point (°C)	Polymethacrylate polymers	Pour point (°C; measured)	Descent in pour point (°C)
PDDMMA1	−20	1	PODMMA1	−22	3
PDDMMA2	−19	0	PODMMA2	−21	2
PDDMMA3	−19	0	PODMMA3	−21	2
PTDMMA1	−40	21	PDDTDMMA	−27	8
PTDMMA2	−26	7	PDDHDMMA	−42	23
PTDMMA3	−20	1	PDDODMMA	−38	19
PHDMMA1	−28	9	PTDHDMMA	−41	22
PHDMMA2	−37	18	PTDODMMA	−31	12
PHDMMA3	−25	6	PHDODMMA	−21	2

Figure 6. PDDHDMMA was made from DDMA, HDMA, and MMA at a molar ratio of 3.5 : 3.5 : 3. The spectra shown in Figure 6 were almost the same except for the peak at 1.26 ppm, which was caused by the protons attached to carbon atoms on the side chains. The intensity of that peak for the PDDHDMMA was between those for PDDMMA and PHDMMA; this indicated that the side chain length of PDDHDMMA was longer than that of PDDMMA and shorter than that of PHDMMA. The molecular weight data are shown in Table II. M_n varied from 31,000 to 49,000, depending on the kind of methacrylate monomer used in the synthesis.

Pour point

The base oil, which had a Saybolt universal second of 150, was used for the pour point experiments. The experiments were performed at least three times, and each mixture to be measured contained the base oil and polymer at a concentration of 0.1 wt %. The average values of the pour points are listed in Table III. The pour point of the pure base oil was −19°C.

Copolymers

The pour point values of most samples decreased relative to that of the pure base oil. The pour point of the base oil decreased by as much as 21°C for PTDMMA, which was polymerized with TDMA and MMA at a molar ratio of 7 : 3, was added. This indicated that the polymethacrylate polymers helped decrease the pour point of the base oil. These results can be explained by the steps presented in Figure 7, which outlines the mechanism of this effect. The paraffin crystals, which are represented by the zigzag lines, appeared and grew in the base oil as the temperature decreased. At this moment, the copolymer molecules, which are represented as the comblike structures, played a role in molecular orientation and the nucleating process.[17] The side chains of the copolymers interacted and cocrystallized with the paraffin, whereas the backbone and polar end

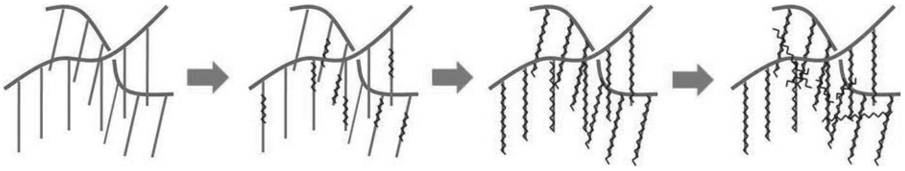

Figure 7 Possible mechanism between the copolymer molecules and paraffin crystals with decreasing temperature.

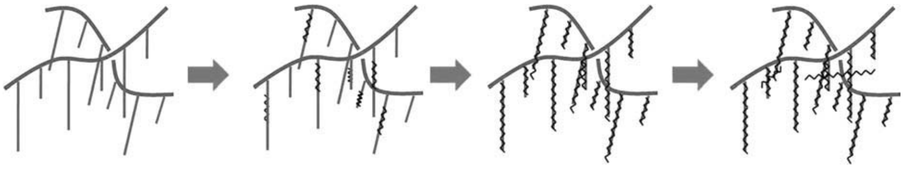

Figure 8 Possible mechanism between the terpolymer molecules and paraffin crystals with decreasing temperature.

groups limited such crystallization.[9,19–22] This prevented the crystals from forming a network and a gel-like structure. Therefore, the pour point of the base oil decreased when the polymethacrylate polymers were added as PPDs.

In addition, we observed that an increase in the molar fraction of the alkyl methacrylate monomer, in general, decreased the pour point values relative to MMA. For example, the molar fractions of TDMA were 0.70, 0.50, and 0.30 in samples PTDMMA1, PTDMMA2, and PTDMMA3, respectively, and the pour points of the base oils containing them were −40, −26, and −20°C, respectively. This result was related to the number of the side chains of the copolymers. The increase in the molar fraction of the methacrylate monomer compared to MMA meant that the number of side chains increased. As the number of the side chains increased, the possibility of cocrystallization with the side chains and paraffin increased; hence, the pour point decreased.

Terpolymers

The pour points of the base oil containing terpolymer were lower than that with copolymer. This means that the terpolymers, made with MMA and two kinds of methacrylate monomers, were better than the copolymers made with MMA and just one monomer. For example, the pour point of the base oil containing PDDHDMMA was −42°C, whereas the pour points were −20°C for PDDMMA and −28°C for PHDMMA. A possible mechanism explaining these results is described in Figure 8. Terpolymers had side chains that were not identical in length (Fig. 8), whereas copolymers had identical side chains (Fig. 7). As presented in Figure 8, there were more spaces among the terpolymer molecules than copolymer molecules because of the different side chain lengths. Therefore, the probability of the formation of network structures among the paraffin crystals cocrystallized with side chains of the terpolymers became lower. Thus, when the temperature decreased more, the paraffin crystals could form networks, and the base oil could not flow.

CONCLUSIONS

Polymethacrylate polymers for use as PPDs were synthesized by free-radical polymerization. Four methacrylate monomers were synthesized by the esterification of MMA and four fatty alcohols. Copolymers, which were synthesized from only one kind of monomer and MMA, and terpolymers, which were synthesized from two kinds of monomers and MMA, were prepared. The pour points of the base oil containing these polymers were measured. The addition of most copolymers decreased the pour point of the base oil. PTDMMA polymerized with TDMA and MMA at a molar ratio of 7 : 3 displayed the best low-temperature properties among all of the ones tested. The pour point of the base oil containing this polymer was −40°C, which meant that it decreased the pour point of the base oil by as much as 21°C. The addition of each of the terpolymers also decreased the pour points of the base oil. When the overall performance of the copolymers were compared with those of the terpolymers, the terpolymers were shown to display better low-temperature properties than the copolymers. Thus, the low-temperature properties of the polymethacrylate polymers were enhanced when two kinds of methacrylate monomers were polymerized together. In the case of PDDHDMMA, which had the most efficient PPD in this study, the pour point of the base oil was −42°C, whereas the pour points were −20°C for PDDMMA and −28°C for PHDMMA, respectively. This result could be explained by a difference in the polymer molecular structure. In addition, the yields of all of the terpolymers were above 93%.

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