

Cyclic Alkyl Ketene Oligomers

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ABSTRACT: Two alkyl ketene oligomers (AKOs) with almost 100% purities were prepared in high yields of 80–90% from palmitic acid chloride and alkyl ketene dimer (prepared from palmitic acid chloride) in the presence of amine promoters. Two AKOs thus obtained had quite similar molecular weights (1000–10,000), carbon/hydrogen contents, X-ray diffraction patterns, solution-state ^{13}C -NMR spectra, and water-contact angles. However, two AKOs had different size-exclusion chromatograms, differential scanning calorimetric curves, FTIR spectra, and solution-state ^{13}C -NMR spectra for ^{13}C -labeled AKOs. Based on the ^{13}C -NMR spectra of ^{13}C -unlabeled AKOs, AKOs are likely to have cyclic structures, thus having the limited molecular weights of <10,000. The results of FTIR spectra and ^{13}C -NMR spectra of ^{13}C -labeled AKOs indicated that three different repeating units were linked with various molar ratios and various connection patterns and combinations, constituting the cyclic AKOs. As a result, ^{13}C -NMR spectra of ^{13}C -labeled AKOs showed quite a number of carbon signals due to various $^{13}\text{C}=\text{O}$ and $^{13}\text{C}=\text{C}$ structures present in AKOs. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3668–3673, 2013

KEYWORDS: dendrimers; hyperbranched polymers and macrocycles; monomers; oligomers and telechelics; structure-property relations

Received 23 February 2013; accepted 3 June 2013; Published online 26 June 2013

DOI: 10.1002/app.39618

INTRODUCTION

Alkyl ketene dimers (AKDs) are synthesized from fatty acid chloride with triethylamine used as a promoter in an organic solvent such as toluene, and each AKD molecule has a unique hetero four-membered ring and two long alkyl chains.¹ The AKD waxes produced at the industrial level generally have AKD contents of >80%, and their aqueous emulsions prepared with surfactants and other additives via heating and homogenization treatments in water have been used as sizing chemicals in paper-making process under neutral/alkaline conditions for more than 40 years. The components other than AKD present in crude AKD waxes are so-called alkyl ketene oligomers (AKOs), fatty acid anhydrides, and fatty acids. Based on the results of size-exclusion chromatography (SEC) and gas chromatographic analysis of commercial AKD waxes, approximate weight ratios of AKOs, fatty acid anhydrides, and fatty acids in the waxes are 7–10%, 5–6%, and 0.3–2%, respectively.^{2,3}

Hardell first prepared an AKO-rich product containing ≈84% AKD oligomers by heating an AKD wax in triethylamine at 90°C for 16 h without further purification, and proposed that AKOs had chemical structures of linear oligoesters consisting of the repeating unit A shown in Figure 1.² Yoshida et al. have prepared cellulose β -ketoesters with degrees of substitution of >2 by reactions of cellulose (dissolved in a non-aqueous cellulose

solvent) with various AKDs (prepared from C12–C18 fatty acid chlorides) in the presence of 1-methylimidazole used as an esterification promoter.^{4–7} The obtained polymer-brush-type cellulose derivatives had unique properties; carbons of cellulose chains and those close to the β -ketoester bonds behave like solids in solution states, because mobility of these carbons are strongly restricted even in solution states, owing to the long alkyl chains densely introduced to cellulose chains. Moreover, it was found that significant amounts of AKOs were formed as by-products from AKDs in the reaction mixtures, and that the formation of these AKOs disturbed efficient β -ketoesterification between cellulose and AKDs.^{4–7}

Thus, according to the literature and our previous studies, two protocols are possible to prepare AKOs, AKO-I and AKO-II. AKO-I is formed as a by-product during AKD synthesis and present as a contaminant in the obtained AKD wax, and AKO-II is formed from AKD during β -ketoesterification of cellulose in the presence of 1-methylimidazole. However, it has been unclear whether these two AKOs are identical or different to each other. If AKOs have linear oligoester structures as proposed by Hardel,² it should be made clear why the molecular weights of AKOs are always limited to be less than 10,000. Thus, it is of significance to make clear the formation mechanism of AKOs and their detailed chemical structures and properties for not only paper chemistry but also for applications of AKOs.

The formation mechanism of oligomers from ketene and dimethyl ketene and their chemical structures have been studied in detail as ketene-derived compounds.^{8–12} It has been proposed that ketenes are converted to mixtures of oligoesters, oligoketones, and oligoacetals, consisting of three repeating units A, B, and C shown in Figure 1, respectively, via cationic polymerization.^{11,12} Moreover, it was reported that dimethyl ketene formed an oligoketone-type cyclic trimer with a metastable six-membered ring during oligomerization under particular conditions.^{10,11} Osanai et al. reported that β -butyrolactone, having a hetero four-membered ring like AKD, was transformed to a cyclic oligomer with a molecular weight of ≈ 500 via enzymatic treatment in organic solvent.¹³ Thus, it is possible that AKDs are preferably transformed to cyclic oligomers under certain conditions.

In this study, two AKOs, AKO-I and AKO-II, with high purities were prepared in high yields from different starting materials under different conditions. These two AKOs had similar carbon/hydrogen contents, X-ray diffraction patterns, water-repellency, and solution-state ^{13}C -NMR patterns, whereas they had different SEC elution patterns, differential scanning calorimetric (DSC) curves, FTIR spectra, and ^{13}C -NMR spectra for ^{13}C -labeled and fractionated AKOs. These results indicate that AKOs have cyclic structures consisting of the three different repeating units A, B, and C shown in Figure 1 but with various molar ratios, and different connection patterns and combinations of the repeating units.

EXPERIMENTAL

Materials

Palmitic-1- ^{13}C -acid chloride ($\text{CH}_3-(\text{CH}_2)_{14}-^{13}\text{COCl}$) was supplied from NOF Co., Japan. Palmitic acid chloride without ^{13}C -labeling, triethylamine, 1-methylimidazole, and other reagents and solvents were of laboratory grade (Wako Pure Chemicals, Co. Ltd., Japan), and used without further purification. Chloroform of liquid chromatography grade (Wako Pure Chemicals, Co., Ltd., Japan) was used as an eluent for SEC.

Preparation of AKOs

Palmitic acid chloride (3.0 g) and triethylamine (1.2 g) were vigorously agitated using a planetary micro ball mill (Pulverisette 7; Fritsch GmbH, Germany) at 800 rpm for 30 min without any temperature control, and the mixture was neutralized using 0.1M HCl and then washed with water several times at approximately 80°C to remove hot-water soluble compounds (mainly triethylamine HCl salt). Tetrahydrofuran (THF) was added to the waxy reaction product, and an AKD/AKO-rich product was obtained as the THF-soluble fraction. The waxy AKD/AKO mixture was extracted several times with ethanol, and the ethanol-insoluble fraction was collected as powdery AKO-rich product (AKO-I) in the yield of 80–90% (based on palmitic acid chloride used as the starting material) after evaporation.

An AKD was synthesized from palmitic acid chloride according to a method reported in the literature.^{1–3} Another AKO was prepared from this AKD (0.1 g) via heating at 90°C for 3 h in the presence of a catalytic amount of 1-methylimidazole (1 μL) used as an oligomerization promoter according to a previously reported method.⁴ The reaction product was purified according

to the same procedure as described previously, and a powdery AKO-rich product (AKO-II) was obtained in the yield of 80–90% (based on AKD used as the starting material).

^{13}C -Labeled AKO-I and AKO-II were prepared from palmitic-1- ^{13}C -acid chloride and ^{13}C -labeled AKD, respectively, according to the procedures to prepare the corresponding unlabeled AKOs, on the assumption that there is no difference in the chemical structure between the ^{13}C -labeled and unlabeled AKOs.

Analyses

Carbon, hydrogen, and nitrogen contents of AKD and AKOs were determined using an elemental analyzer. FTIR spectra were collected for thin film samples using a MAGNA-IR 860 (Madison, WI). Solution-state ^{13}C -NMR spectra of the products were collected on a JEOL ALPHA 500 spectrometer (JEOL, Japan), in which CDCl_3 or benzene- d_6 was used as the solvent. Tetramethylsilane was used as an internal standard. The AKD and AKO samples were pressed to pellets, and were subjected to X-ray diffraction analysis using a Rigaku RINT 2000 with a monochromator-treated Cu K α radiation (wavelength 0.15418 nm) at 40 kV and 40 mA by the diffraction method. Water repellency of the AKO samples was evaluated by measuring contact angles of water droplet (2.0 μL) put on AKO film surfaces (prepared from AKO/chloroform solutions via casting and drying) at 100 ms after the water-droplet landing (Kyowa Interface Science Co. Ltd., Japan). Water-contact angles were measured in a conditioning room at 23°C and 50% relative humidity, and expressed as an average value of five measurements for each sample. Thermal properties of the samples were determined by means of a Perkin–Elmer differential scanning calorimeter from 25 to 150°C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere.

Determination of molecular weights and molar-weight distributions of the original and fractionated AKOs were carried out using a SEC system with chloroform as an eluent. Fractionation of AKOs with narrow molecular weight distributions from the original AKOs was also performed using the SEC system. The SEC system consisted of an on-line degasser (DGU-12A; Shimadzu, Japan), a high-pressure pump (LC-10ADVP; Shimadzu, Japan), a stainless steel inline filter with poly(tetrafluoroethylene) (PTFE) membrane (0.1 μm pore size, Millipore, USA), an automatic injector (SIL-20A; Shimadzu, Japan), a column oven (CTO-10ACVP; Shimadzu), and a refractive index detector (RID-10A; Shimadzu, Japan). Two SEC columns (8 ϕ \times 300 mm; K-802.5 and 20 ϕ \times 300 mm; K2002.5) (Shodex, Japan) packed with a styrene-divinylbenzene copolymer gel were used for SEC analysis and SEC-fractionation, respectively. Data acquisition and processing were carried out with poly(styrene) standards using the ASTRA software (Wyatt technologies, USA). The SEC conditions were as follows: sample concentration of 1.0% (wt/vol), injection volumes of 20 and 200 μL for SEC analysis and SEC fractionation, respectively, flow rate of 2 mL min⁻¹, and column temperature of 40°C.

RESULTS AND DISCUSSION

Preparation of AKOs

Both the original AKO-I and AKO-II were obtained as powdery solids in high yields of 80–90% based on the starting materials.

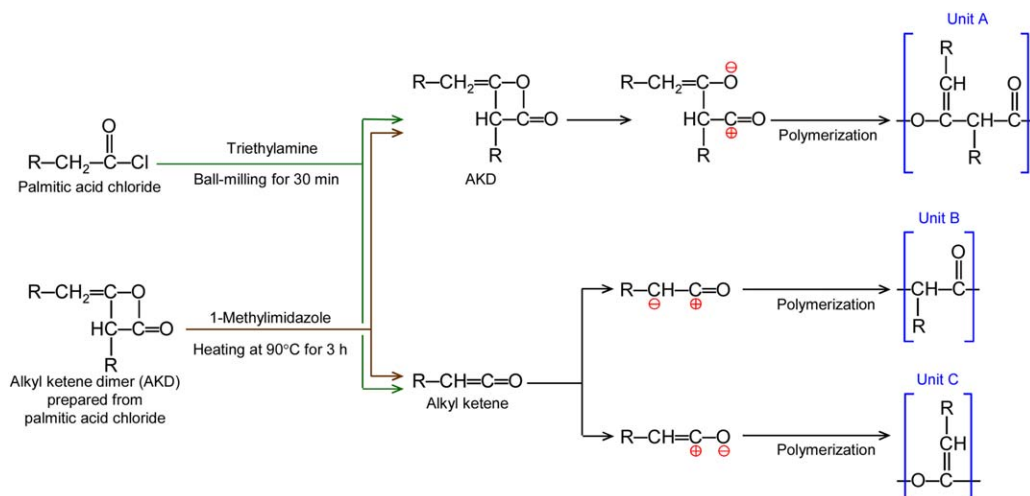


Figure 1. Possible structures of AKOs consisting of three different repeating units, A, B, and C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

The SEC elution patterns of AKD, AKO-I, and AKO-II are shown in Figure 2. The AKD sample prepared from palmitic acid chloride had a main peak at 49.6 mL elution volume, which corresponds to a molecular weight of 476 ($C_{32}H_{60}O_2$). Small peaks due to AKO components were detected in the SEC elution pattern at 40–48 mL elution volume; the synthesized AKD contained a small amount of AKOs.^{2,3}

In contrast, both AKO-I and AKO-II had wide molecular weight distributions at 38–50 mL elution volumes, which corresponded to 10,000–1000 molecular weights, when poly(styrene) standards were used in calibration. Thus, the two procedures used in this study provided almost pure AKOs in high yields on the basis of the SEC elution patterns. However, AKO-I and AKO-II had explicitly different SEC elution patterns and molecular weights. Each AKO had one main peak and 2–3 sub-peaks, but they appeared at different elution volumes between two AKOs. The

main peak positions in the SEC elution patterns showed that AKO-II had a molecular weight higher than that of AKO-I.

Properties of AKOs

The DSC curves of AKD, AKO-I, and AKO-II are shown in Figure 3. AKD has an endothermic peak at $\approx 50^\circ\text{C}$ due to its melting point, which is consistent with those reported in the literature.^{3,14} On the other hand, the AKO-I had broad and multiple peaks in the range from 35 to 60°C , and the AKO-II had those in wider range from 35 to 70°C , indicating that AKO-I and AKO-II consisted of different AKO components to each other. Because AKO-II had a higher molecular weight and a wider molecular weight distribution than AKO-I (Figure 2), the relatively large endothermic peaks of AKO-II at $50\text{--}70^\circ\text{C}$ are likely to be due to AKO components with higher molecular weights. The DSC curves in Figure 3 were obtained in the first heating runs, and almost the same DSC curves were obtained also in the second heating runs.

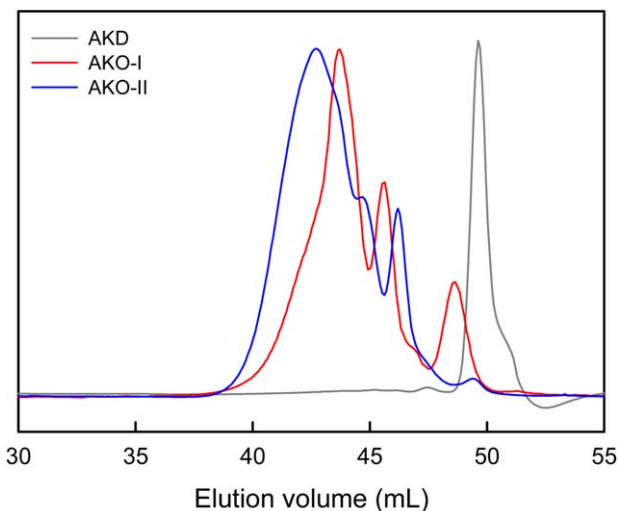


Figure 2. SEC elution patterns of AKD and two alkyl ketene oligomers (AKO-I and AKO-II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

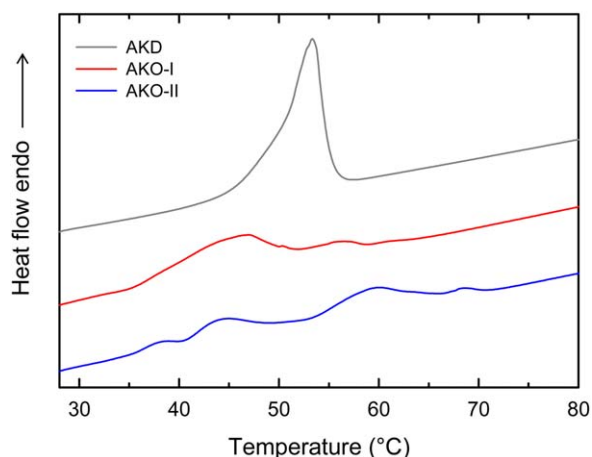


Figure 3. DSC curves of AKD and two alkyl ketene oligomers (AKO-I and AKO-II) in the first heating run. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

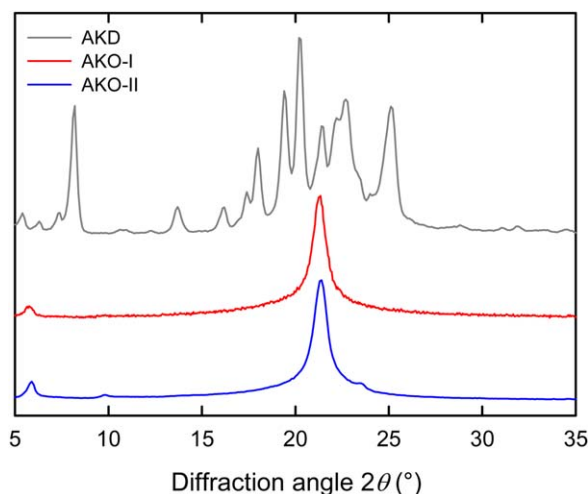


Figure 4. X-ray diffraction patterns of AKD and two alkyl ketene oligomers (AKO-I and AKO-II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

X-ray diffraction patterns of AKD, AKO-I, and AKO-II are depicted in Figure 4. AKD was a crystalline compound, and had multiple diffraction peaks,^{3,14} whereas both AKO-I and AKO-II had only two peaks at diffraction angles of 5.8° and 21.4°, and had more disordered structures than AKD. These two diffraction peaks of AKOs corresponded to the alkyl chain length (1.5 nm) and hexagonal packing pattern of alkyl chains (0.41 nm), respectively, indicating that both AKOs had almost disordered structures except the long alkyl chain parts. The results obtained in Figure 4 are consistent with those in Figure 3, because endothermic peaks of AKOs with disordered structures (probably due to glass transition and some phase-transitions) started from 35°C, which was lower than the melting point of crystalline AKD.

The water-contact angles on the AKO films were measured for evaluation of their hydrophobic nature (Figure 5). Both AKOs had almost the same water-contact angles of 116–117°, which is similar to that of paraffin.¹⁵ Thus, the hydrophobic nature of AKOs is primarily due to long alkyl chains of AKOs, and connection parts of repeating units containing oxygen atoms (Figure 1) may have no contribution to the water-contact angles of the AKO films; probably the surface of AKO films are covered with long alkyl chains alone. As a result, although both AKO-I and AKO-II had similar disordered structures and the film surfaces were similarly covered with long alkyl chains of AKOs, these two AKOs probably consisted of different AKO components, resulting in the different SEC elution patterns or DSC curves to each other.

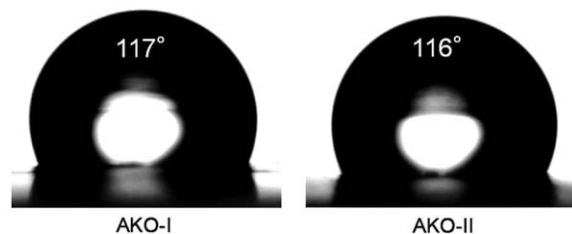


Figure 5. Photographs of water droplets on two alkyl ketene oligomer films (AKO-I and AKO-II), and their water-contact angles.

Table I. Carbon, Hydrogen, and Nitrogen Contents of AKD and Two Alkyl Ketene Oligomers (AKO-I and AKO-II)

Sample	Carbon	Hydrogen	Nitrogen
AKD	81.1	12.9	0.0
AKO-I	83.2	12.3	0.0
AKO-II	79.9	12.0	0.0

Structures of AKOs

The carbon and hydrogen contents of AKD, AKO-I, and AKO-II are listed in Table I. It was confirmed that neither triethylamine nor 1-methylimidazole used as the oligomerization promoters existed in AKOs. Even though small differences in carbon or hydrogen content were observed between the three samples, these differences might be within experimental errors; the three compounds had nearly the same carbon and hydrogen contents. According to the connection patterns and combinations of the three repeating units shown in Figure 1, there is no rational explanation that these three compounds have different carbon or hydrogen contents.

As shown in Figure 2, the original AKOs were mixtures of various AKO components with different molecular weights, which will make the structural analysis of AKOs difficult. Then, the original AKOs were fractionated using the SEC system to prepare AKOs with narrow molecular weight distributions. Figure 6 shows SEC elution patterns of AKD and two fractionated AKOs. The fractionated AKOs had polydispersity values as small as ≈ 1 , and thus the fractionation was successfully achieved, although yields of the fractionated AKOs were not determined in this study. These AKOs were estimated to have molecular weights of ≈ 5000 , when poly(styrene) standards were used in the molecular weight calculation. These molecular weights corresponded to approximately 10 repeating units of Unit-A or 20 repeating units of Unit B and/or Unit C shown in Figure 1.

The ¹³C-NMR spectra of AKD and two fractionated AKOs are presented in Figure 7. AKD showed a typical ¹³C-NMR

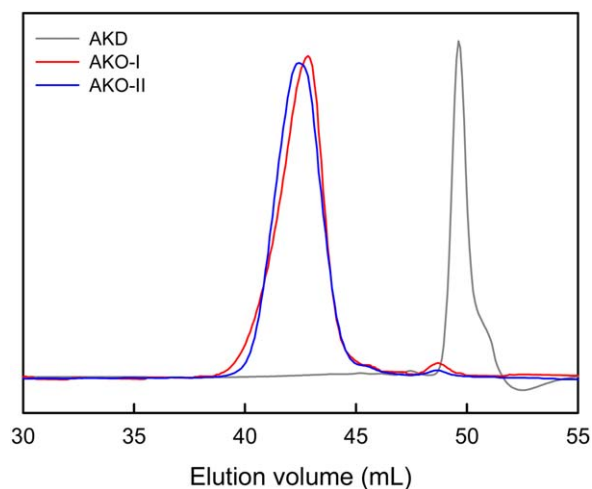


Figure 6. SEC elution patterns of AKD and two alkyl ketene oligomers (AKO-I and AKO-II) prepared from the original AKOs by fractionation using SEC system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

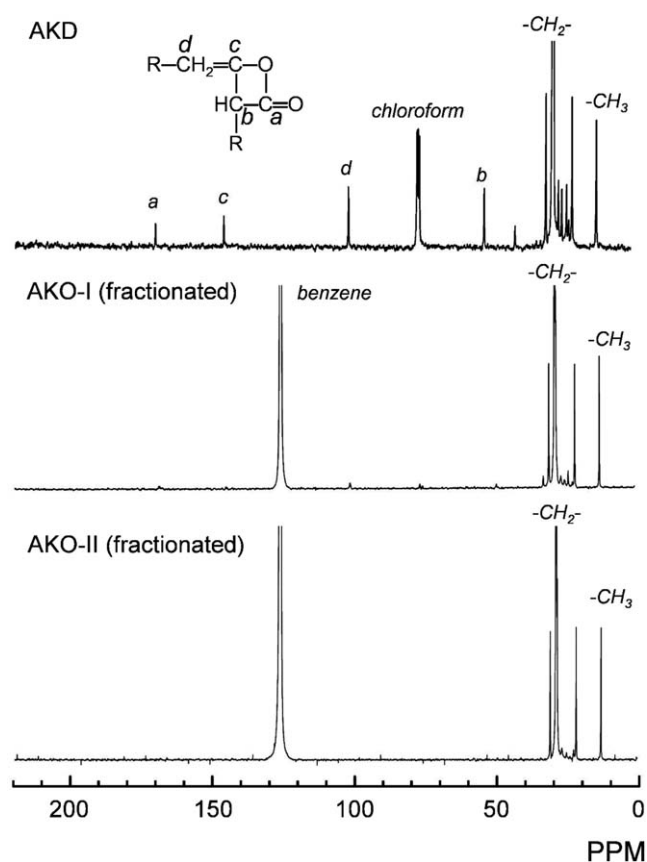


Figure 7. ^{13}C -NMR spectra of AKD and two fractionated alkyl ketene oligomers (AKO-I and AKO-II).

spectrum, which had all carbon signals due to the four-membered ring. In contrast, only carbon signals due to alkyl chains were observed in the ^{13}C -NMR spectra of AKOs, and no signals due to carbons close to connection parts of the repeating units were detected in the spectra. These NMR spectra of AKOs gave a false impression that AKOs had chemical structures of simple alkanes without any carbonyl groups or double bonds. These solution-state ^{13}C -NMR spectra of AKOs are very similar to those of polymer-brush-type cellulose β -ketoesters with degrees of substitution of >2 prepared from cellulose via homogeneous reaction with AKDs.^{4–7} In the case of the polymer-brush-type cellulose β -ketoesters, cellulose molecules and β -ketoester parts (except long alkyl chains) behave like solid even in solution state owing to strong restriction in their mobility via the densely introduced long alkyl chains into cellulose molecules.^{4–7}

The results of solution-state ^{13}C -NMR spectra of AKOs also indicated that the connection parts of the repeating units were strongly restricted in mobility. If AKOs have linear chemical structures consisting of the repeating units, some carbon signals due to both ends of oligomer chains should be detected in the ^{13}C -NMR spectra. This is because carbons of both ends are not plausible to be restricted in mobility in the solution state. Hence, AKOs prepared in this study are likely to have cyclic structures consisting of various ratios of the three repeating units shown in Figure 1, and molecular weights of AKOs are thus limited to be less than 10,000.

Solution-state ^{13}C -NMR analysis of AKOs was further carried out using ^{13}C -labeled and fractionated AKOs to detect signals due to carbons close to connection parts of AKO repeating units. Detection sensitivity of ^{13}C -labeled carbons can increase to approximately 100 times as much as that of normal ^{12}C -rich carbons. Expectedly, the carbon signals due to $^{13}\text{C}=\text{O}$ and $^{13}\text{C}=\text{C}$ in AKOs were detected in the range of 135–210 ppm (Figure 8), and various large and small carbon signals were observed in this region. Thus, ^{13}C -labeled AKO-I and AKO-II had clearly different ^{13}C -NMR patterns, although the spectra of unlabeled AKOs were almost identical to each other (Figure 7). These results showed that two AKOs had different molar ratios and connection patterns and combinations of the three repeating units shown in Figure 1, although they had similar molecular weights and X-ray diffraction patterns. Moreover, it is possible for AKOs to have some isomeric structures of the repeating units (Figure 1), which may also have made the NMR patterns in Figure 8 more complicated.

Although detailed and accurate definition of chemical structures of two fractionated AKOs was difficult at present, the NMR patterns revealed that AKO-I had heterogeneous structures with $^{13}\text{C}=\text{O}$ groups primarily due to esters (with small amounts of ketones), and had various types of ester $^{13}\text{C}=\text{O}$ and $^{13}\text{C}=\text{C}$ groups. In contrast, AKO-II had more simple and homogeneous structures, and had $^{13}\text{C}=\text{O}$ groups due to both esters and ketones, and $^{13}\text{C}=\text{C}$ groups. It is possible that the $\text{C}=\text{O}$ group in Unit B shown in Figure 1 exists as not only esters (by connecting with either Unit A or C) but also ketones (by connecting with the same Unit B) in AKOs. Furthermore, the $\text{C}=\text{O}$

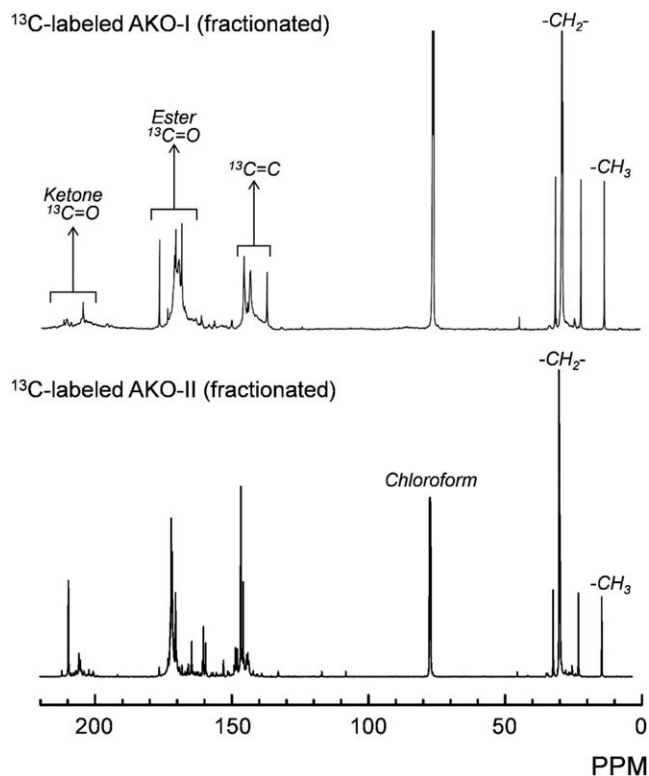


Figure 8. ^{13}C -NMR spectra of the fractionated alkyl ketene oligomers (AKO-I and AKO-II) prepared from ^{13}C -labeled palmitic acid chloride.

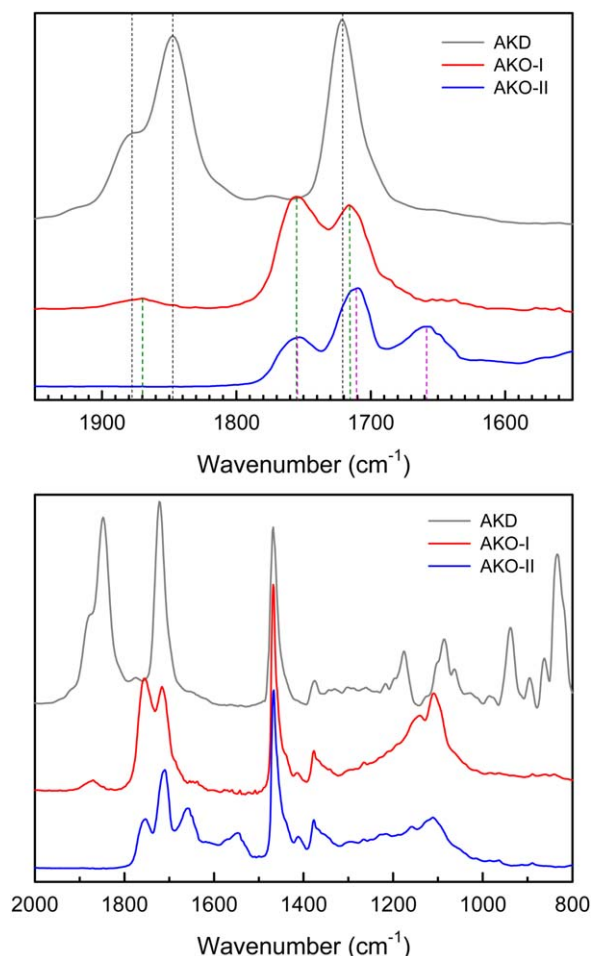


Figure 9. FTIR spectra of AKD and two fractionated alkyl ketene oligomers (AKO-I and AKO-II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

group in Unit A is possible to exist as not only esters (by connecting with either Unit A or C) but also ketones (by connecting with Unit B) in AKOs.

Structures of the two fractionated AKOs were further investigated using their FTIR spectra (Figure 9). The spectrum of AKD had two typical bands at 1722 and 1846 cm^{-1} (with a shoulder at 1876 cm^{-1}) due to the C=C and C=O stretching vibrations, respectively.^{4–7} In contrast, the FTIR spectra of AKO-I and AKO-II were significantly different from the AKD spectrum. Moreover, two AKOs had explicitly different patterns to each other in the region of 1500–1900 cm^{-1} , whereas they had quite similar patterns at 800–1500 cm^{-1} . This result also supports the hypothesis that two AKOs had similar chemical structures but different molar ratios and connection patterns and combinations of the three repeating units shown in Figure 1.

Based on the results in Figure 8 and the literature,^{10,11} the two absorption bands at 1716 and 1755 cm^{-1} for AKO-I are probably attributed to the ester C=O and C=C stretching vibrations (of Units A and C), respectively. Because the small band at 1870 cm^{-1} in the spectrum of AKO-I was not identical to that of AKD (Figure 9), this band is also characteristic for AKO-I. In

contrast, AKO-II had additional bands at 1547 and 1709 cm^{-1} , and the relative absorption intensities at ≈ 1710 and ≈ 1750 cm^{-1} were different between the two AKOs. Moreover, the peak position of the band at ≈ 1710 cm^{-1} was slightly different to each other: 1716 and 1709 cm^{-1} for AKO-I and AKO-II, respectively. The ketone-rich structures of AKO-II (Figure 8) may have caused the FTIR spectrum different from that of AKO-I, although details are unknown.

CONCLUSIONS

Almost pure AKOs, AKO-I and AKO-II, were synthesized in high yields of $\approx 80\%$ from palmitic acid chloride and AKD (prepared from palmitic acid chloride), respectively, under different conditions. Both AKOs had molecular weights in the region from 1000 to 10,000, and had similar carbon/hydrogen contents, X-ray diffraction patterns, ^{13}C -NMR spectra for ^{13}C -unlabeled samples, and water-contact angles. In contrast, two AKOs had different SEC-elution patterns, DCS curves, ^{13}C -NMR spectra for ^{13}C -labeled samples, and FTIR spectra in the regions due to C=O and C=C bands. Because ^{13}C -NMR spectra of the ^{13}C -unlabeled AKOs showed no carbon signals due to either both ends or connection parts of the repeating units, AKOs were likely to have cyclic structures. However, the molar ratios and connection patterns and combinations of the three repeating units are various and different between the two AKOs, resulting in the above differences between two AKOs.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of Grand-in-Aid for Scientific Research (Grant number 19-4572 and 15658052) from the Japan Society for the Promotion of Science (JSPS).

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