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Convenient Synthesis of Polymers Containing Labile Bonds in the Main Chain by Radical Alternating Copolymerization of Alkyl Sorbates with Oxygen

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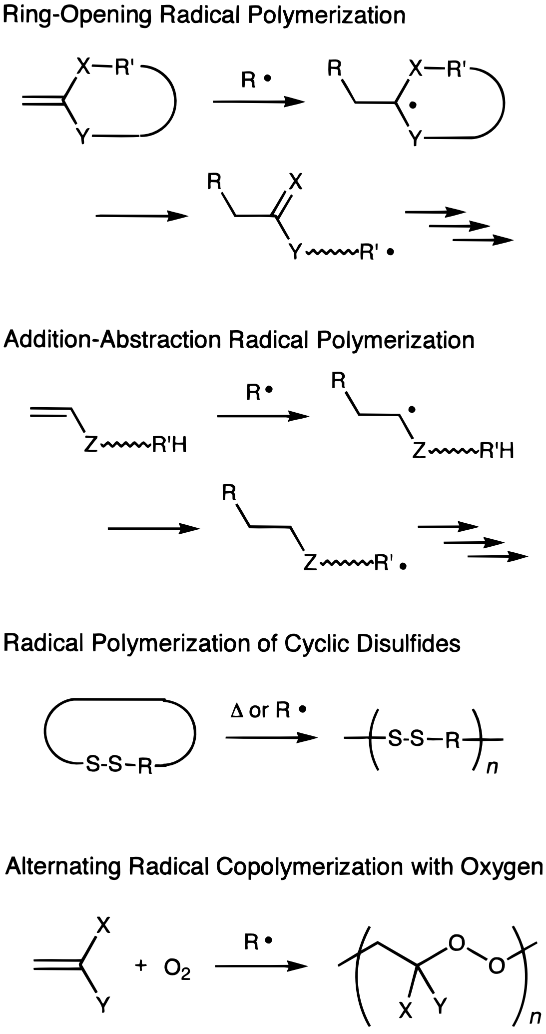
ABSTRACT: The alternating copolymer of alkyl sorbates with oxygen was prepared by photopolymerization or thermal polymerization in the presence of oxygen. Methyl sorbate provided an alternating copolymer with oxygen on exposure to sunlight at room temperature. The yield and molecular weight of the obtained polymers depended on the polymerization conditions, e.g., the ester alkyl groups, the polymerization temperature, and the kinds of solvents. NMR spectroscopy confirmed the alternating copolymer structure containing labile peroxy bonds in their main chain. It was revealed by gel permeation chromatography that the polymers readily decomposed on heating. The molecular weight of the polymer was reduced to half value after 12 h at 60 °C, and the polymer immediately degraded to low molecular weight products at 120 °C.

Introduction

The radical polymerization of vinyl monomers provides polymers consisting of a substituted polyethylene structure, of which the main chain is successive carbon-to-carbon bonds. Functional groups or heteroatoms are readily introduced in the side chains of vinyl polymers but not inserted into the main chain skeletons except for the following several cases (Scheme 1): ring-opening polymerization,[1] addition−abstraction polymerization,[2] the polymerization of cyclic disulfides,[3] and the copolymerization of vinyl monomers with a non-vinyl-type monomer including molecular oxygen.[4] Especially, the copolymerization of vinyl monomers with oxygen is the most simple method and applied to a variety of monomers. For example, the oligomer formation of styrene and α-methylstyrene with oxygen was reported several tens of years before.[5] The mechanistic studies of the copolymerization have been carried out as well as some applications of the resulting copolymers which has potential for the use as a macroinitiator, a special fuel, and curatives in coating and molding.[6]

Scheme 1



In the course of our recent research on the topochemical polymerization of diene monomers such as muconic and sorbic acid derivatives,[7] we found that octadecyl sorbate (ODS) polymerizes in the crystalline state in the presence of oxygen under UV irradiation to give an alternating copolymer.[8] The copolymerization reactivity and the structure of the resulting copolymer depended on the recrystallization solvents for the preparation of monomer crystals and on the polymerization atmosphere. In this solid-state copolymerization, the reaction path and reactivity were controlled by the crystal lattice, but the polymerization did not proceed via a topochemical mechanism. The crystals of ODS collapsed during the copolymerization, in contrast with the topochemical polymerization of muconic acid derivatives yielding tritactic polymers, which were isolated as the polymer crystals. Recently, we have noticed that similar alternating copolymers with oxygen are conveniently pre-

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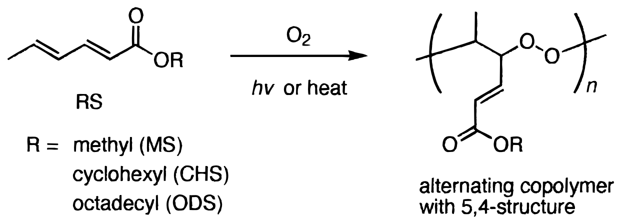
Scheme 2



pared not only by solid-state photopolymerization of ODS but also by isotropic polymerization of several alkyl sorbates (RS) other than ODS under various conditions. In this paper, we describe the facile synthesis of the alternating copolymers from RS with oxygen by photopolymerization and thermal polymerization (Scheme 2). The degradation of the resulting copolymers was also investigated.

Experimental Section

Materials. Commercial methyl sorbate (MS, Tokyo Chemical Industries, Japan) was distilled under reduced pressure (bp 42 °C/5 mmHg). Cyclohexyl sorbate (CHS) was prepared from sorbic acid and cyclohexanol in the presence of H_2SO_4 in toluene with reflux for 10 h, followed by distillation under reduced pressure (bp 100 °C/5 mmHg). Octadecyl sorbate (ODS) was prepared by the method previously reported,[8] followed by recrystallization from ethanol (mp 38−39 °C).

MS: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, $J = 15.2$ and 9.6 Hz, 1H, CH=), 6.08−6.23 (m, 2H, CH=), 5.77 (d, $J = 15.2$ Hz, 1H, CH=), 3.73 (s, 3H, OCH_3), 1.85 (d, $J = 6.4$ Hz, 3H, CH_3). CHS: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, $J = 15.2$ and 9.6 Hz, 1H, CH=), 6.07−6.22 (m, 2H, CH=), 5.78 (d, $J = 15.2$ Hz, 1H, CH=), 4.48−4.55 (m, 1H, OCH), 1.2−2.0 (m, 13H, CH_2 and CH_3).

2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. The solvents were distilled before use.

Polymerization. RS was charged in a Pyrex glass tube and polymerized with bubbling of O_2, air, or N_2 under irradiation of UV light using a high-pressure mercury lamp (Toshiba SHL-100-2) or sunlight. After the polymerization, a reaction mixture was poured into a large amount of precipitant (hexane, methanol, and ethanol for the polymerization of MS, CHS, and ODS, respectively) to isolate the resulting polymer. The polymer yield was determined gravimetrically.

Measurements. Number- and weight-average molecular weight (M_n and M_w) were determined by gel permeation chromatography (GPC) in tetrahydrofuran as an eluent using a Tosoh GPC-8000 series system and calibrated with standard polystyrenes. NMR and IR spectra were recorded on a JEOL JNM-A400 and JASCO FT-IR-430 spectrometer, respectively.

Results and Discussion

The results of the photopolymerization of RS in bulk under various conditions are summarized in Table 1. During the photoirradiation using a high-pressure mercury lamp in the presence of O_2 or air at various temperatures, MS provided a polymer, of which the M_n and M_w/M_n values were $(1-3) \times 10^3$ and 1.8−2.3, respectively, in 16−71% yield. Here, the polymer yield was calculated on the basis of the amount of RS charged. The polymer obtained from the polymerization of MS in the presence of O_2 was colorless and tacky, being miscible with common organic solvents except *n*-hexane. In the ^{1}H NMR spectrum of the polymer shown in Figure 1, the characteristic peaks of vinylene protons as the pendant in the side chains were observed at 6.1 and 6.9 ppm as well as the splitting peaks at 4−5 ppm due to the methine protons in the main chain. The spectrum is very close to that of the copolymer prepared by solid-state photopolymerization of ODS previously reported,[8] being assigned to be an alternating copolymer of RS with O_2 with a 5,4-structure as the repeating unit, as shown in Scheme 2.

The polymer yield increased with the photoirradiation time during the polymerization of MS in the presence of O_2 at 60 °C, while the M_n value decreased with the time. Figure 2 shows the GPC elution curves of the copolymers produced by the copolymerization of MS with O_2 under photoirradiation at 60 °C. The copolymer isolated from the 4 h polymerization provided a bimodal molecular weight distribution, while the 10 h irradiation resulted in the formation of a unimodal molecular weight copolymer with a lower molecular weight. The M_n and M_w/M_n values varied from 2.6×10^3 and 1.9 to 2.1×10^3 and 1.7, respectively, for each polymer obtained from the 4 and 10 h polymerization.

The polymer yield also depended on the polymerization temperature. While the higher molecular weight polymer was produced during the polymerization at 30 °C, an increase in the polymerization temperature decreased the M_n value of the resulting polymers. The polymerization proceeded even when MS was exposed to sunlight in air at room temperature to give a polymer in 29% yield. In contrast with the polymer formation in the presence of O_2, a trace amount of the polymer was produced under a nitrogen atmosphere.

When the copolymerization of RS with O_2 was carried out in the dark in the presence of AIBN as a radical initiator at 60 °C, the copolymer was obtained similarly to the photopolymerization. Unexpectedly, the copolymer was produced in 36% yield even when MS was heated at 60 °C in the dark without using AIBN. These results indicate that the copolymerization of MS with O_2 proceeds irrespective of the kind of stimulus for initiation, i.e., photopolymerization or thermal polymerization in the presence or absence of an initiator. Simultaneously, it is also evidenced that the propagation is not related to the photoirradiation.

Differing from the facile alternating copolymerization of MS with O_2 irrespective of the polymerization conditions, it was found that successive units of RS were included in the polymers produced by the polymerization of CHS and ODS with O_2 under similar conditions. The homopolymerization reactivity decreased in the order ODS $\gg$ CHS > MS in the polymerization under N_2 atmosphere,[9] suggesting the difficulty of the controlled structure of the alternating copolymers of CHS or ODS with O_2 in bulk polymerization. Furthermore, the viscosity of the reaction medium was increased during the bulk polymerization, resulting in the difficulty of a sufficient supply of O_2 in the cases of CHS and ODS, of which the viscosities are high even at zero conversion. Therefore, the solution polymerization was investigated. Table 2 shows the results of the photopolymerization of MS or CHS with O_2 in several kinds of solvents. It was revealed that not only MS but also CHS provided alternating copolymers and that the polymer yield significantly depended on the kind of solvent. The polymerization proceeded at a greater rate in polar and halogen-containing solvents; the yield decreased in the order CCl_4 > 1,2-dichloroethane > 1,4-dioxane > toluene > *n*-heptane for the copolymerization of MS with O_2. The polymer yield depended on the temperature; i.e., it decreased to 5−13% depending on the solvents when polymerized at 0 °C. During the solution polymerization at a low temperature, the resulting polymers had lower

Table 1. Photopolymerization of RS in Bulk under Various Atmospheric Conditions[a]

RS	atmosphere	stimuli	temp, °C	time, h	yield,[b] %	M_n[c] × 10^{-3}	M_w/M_n[c]
MS	O_2	*hν* (Hg lamp)	30	6	16.3	2.6	1.8
	O_2	*hν* (Hg lamp)	60	4	40.0	2.6	1.9
	O_2	*hν* (Hg lamp)	60	6	56.4	2.5	2.2
	O_2	*hν* (Hg lamp)	60	10	64.0	2.1	1.7
	O_2	*hν* (Hg lamp)	90	6	70.6	1.0	1.9
	air	*hν* (Hg lamp)	60	6	41.1	0.9	2.3
	air	*hν* (sunlight)	r.t	6	29.3	2.2	1.6
	N_2	*hν* (Hg lamp)	60	6	1.1	4.3	1.9
	air	AIBN[d] (in dark)	60	6	24.4	2.0	1.9
	O_2	none (in dark)	60	6	36.3	4.6	1.5
CHS	O_2	*hν* (Hg lamp)	60	6	12.5	2.8	3.1
	N_2	*hν* (Hg lamp)	60	6	3.1	12.2	1.8
ODS	O_2	*hν* (Hg lamp)	60	6	65.4	7.6	2.2
	N_2	*hν* (Hg lamp)	60	6	37.7	12.1	1.4

[a] Polymerization was carried out in a Pyrex tube with bubbling of O_2, N_2, or air into RS in bulk. The photoirradiation was carried out with a high-pressure mercury lamp or under sunlight. [b] The yield was calculated based on the amount of RS charged. [c] M_n and M_w/M_n were determined by GPC calibrated with standard polystyrenes. [d] 2,2′-Azobis(isobutyronitrile), [RS]/[AIBN] = 100.

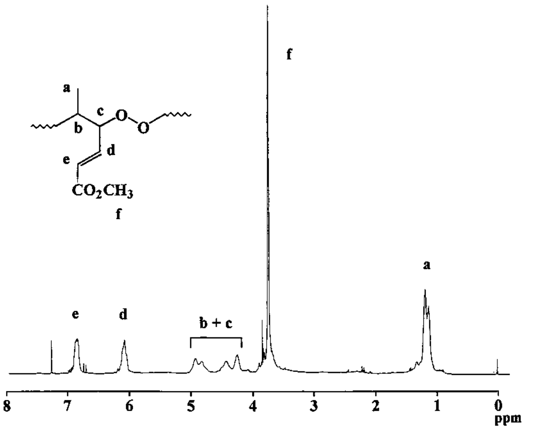


Figure 1. ^1H NMR spectrum of the alternating copolymer of MS with oxygen obtained from bulk polymerization at 30 °C under photoirradiation with a Hg lamp.

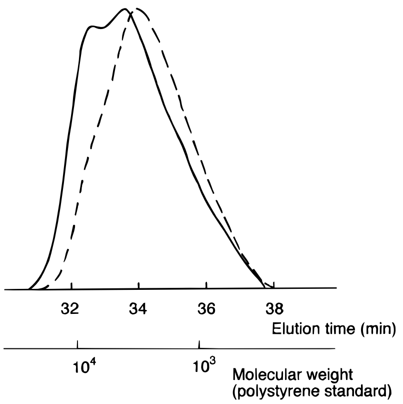


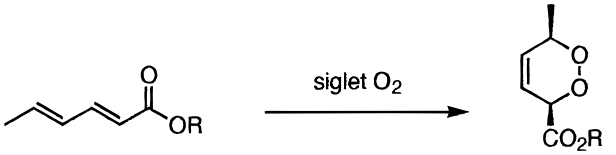
Figure 2. GPC elution curves for the copolymer of MS with oxygen obtained for the polymerization at 60 °C. Polymerization time: 4 h (solid line) and 10 h (dotted line). Columns: TSK G7000H-HR, G6000H-HR, G4000H-HR, G2000H-HR (Tosoh).

Table 2. Photopolymerizations of RS in Various Solvents in the Presence of O_2 under Irradiation with a High-Pressure Mercury Lamp for 6 h[a]

RS	temp, °C	solvent	yield, %	M_n × 10^{-3}	M_w/M_n
MS	30	carbon tetrachloride	46.8	1.1	1.5
		1,2-dichloroethane	42.6	2.1	1.6
		1,4-dioxane	35.7	1.1	1.9
		toluene	28.5	1.8	1.5
		n-heptane	17.2	2.0	1.6
MS	0	carbon tetrachloride	13.0	1.3	1.6
		1,2-dichloroethane	10.8	1.9	1.6
		1,4-dioxane	11.0	1.5	1.5
		toluene	7.3	1.1	1.8
		n-heptane	5.0	1.9	1.4
CHS	30	carbon tetrachloride	11.8	3.1	1.3
		1,2-dichloroethane	7.6	2.8	1.4
		1,4-dioxane	2.3	2.8	1.4
		toluene	1.2	2.7	1.4

[a] RS/solvent = 1/3 in volume. The yields were calculated based on the amount of RS charged.

Scheme 3



M_w/M_n values (M_w/M_n = 1.4−1.9) compared with that of the polymer produced during the bulk polymerization at 60 °C (M_w/M_n ∼ 2).

There are some possible reasons for the solvent-dependent polymerization: (i) the increasing solubility of O_2 in polar solvents, (ii) the elongation of the lifetime of the singlet at an excited state in halogen-containing solvents such as CCl_4, and (iii) the acceleration of the polymerization due to radical formation from the solvent molecule under photoirradiation. It is likely that excess O_2 is present in the solution polymerization systems under the present conditions, judging from the alternating copolymer formation irrespective of the kind of solvent. Regarding case ii, if the polymerization is initiated by singlet oxygen at an excited state, but not the triplet at the ground state, the lifetime in the excited state would influence the rate of the initiation. However, no adduct was produced under our conditions, despite the fact that the singlet oxygen reacted with RS to give a cyclic adduct in a quantitative yield (Scheme 3).[10] We also checked the addition effect of rose bengal as a typical sensitizer, from which the energy is transferred to the ground-state triplet oxygen to generate efficiently an excited-state singlet oxygen, on the photopolymerization system of MS with O_2. However, only an alternating polymer was obtained as the photoproduct. Therefore, the propagation of O_2 is assumed to proceed via the ground-state triplet oxygen, and the lifetime at the excited state is not important for the initiation and propagation during the copolymerization. The fact that the alternating copolymerization is induced not only photochemically but also by heating strongly supports

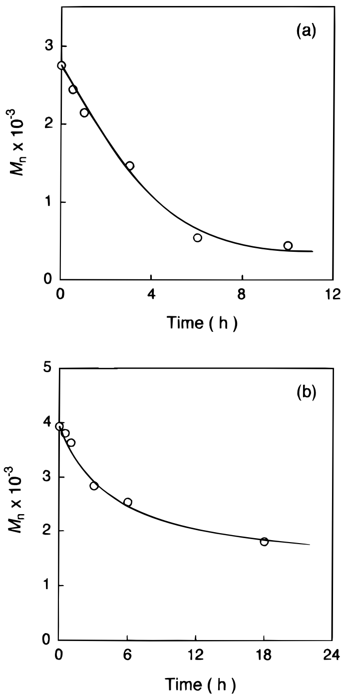


Figure 3. Change in the molecular weight for the copolymers of MS with oxygen during (a) photoirradiation at room temperature and (b) heating at 60 °C in argon.

this conclusion. On the other hand, many radical chain reactions that are photochemically induced have been reported. The free radicals formed by the decomposition of the solvents may initiate polymerization by the addition to MS.

The change of the molecular weight distribution during the polymerization (as already shown in Figure 2) suggests that the degradation of the copolymer occurred simultaneously. Therefore, the degradation of the copolymer was examined by two kinds of stimuli, i.e., photodecomposition and thermal decomposition. When the copolymer was irradiated with a high-pressure mercury lamp with a Pyrex filter at 30 °C, the molecular weight of the copolymer decreased slowly. The peroxy linkage hardly decomposed even under the photoirradiation because the Pyrex glass cuts off light with a wavelength shorter than 280 nm. Therefore, the polymer was directly irradiated without any filters, and the decomposition behavior was monitored as a function of the irradiation time. As shown in Figure 3a, the M_n value of the polymer decreased during the irradiation.

In contrast, the facile thermal decomposition of the copolymer was observed on heating in the dark under argon atmosphere. The change in the molecular weight distribution during the thermal degradation at 120 °C monitored by GPC without any isolation of the products is shown in Figure 4. It is clear that the copolymers degraded to small molecular weight products during the heating for 1 h. The degradation of the copolymer proceeded slowly at 60 °C (Figure 3b). The M_n value of the copolymer decreased from 4×10^3 to 2×10^3 after 18 h heating, indicating that the average number of the scissions of the polymer chain is approximately unity under the present conditions.

When the volatile fraction of thermal decomposition products was trapped and examined by NMR spectroscopy, a main product was revealed to be fumaraldehyde monomethyl ester. A proposed mechanism for the decomposition of the copolymer is shown in Figure 5. In this mechanism, the peroxide linkage in the main chain is cleaved on heating to produce oxygen-centered radicals at the first step of the reactions. These radicals possibly participate in hydrogen abstraction or β-scission. The latter reaction results in the formation of fumaraldehyde monomethyl ester.[11]

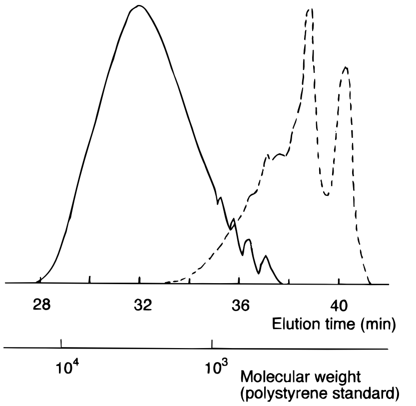


Figure 4. Change in the GPC elution curves for the copolymer of MS with oxygen during thermal degradation at 120 °C for 1 h. Before (solid line) and after degradation (dotted line). Columns: TSK G6000H-HR, G4000H-HR, G3000H-HR, G2000H-HR (Tosoh).

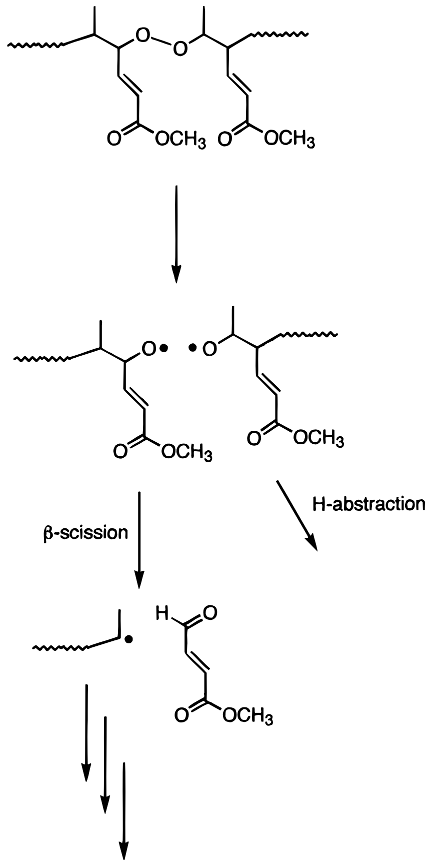


Figure 5. A proposed mechanism for the decomposition of the copolymer of MS with oxygen.

In conclusion, an alternating copolymer of alkyl sorbates with oxygen was prepared by photopolymerization or thermal polymerization in the presence of oxygen. Especially, methyl sorbate provided an alternating copolymer with oxygen under the convenient conditions, e.g., on exposure to sunlight at room temperature. The yield and molecular weight of the obtained polymers depended on the polymerization conditions, e.g., the ester alkyl groups, the polymerization temperature, and the kind of solvent. NMR spectroscopy confirmed the alternating copolymer structure containing labile peroxy bonds in their main chain. Gel permeation chromatography revealed that the polymers readily decomposed on heating. Some applications of the labile polymers are continuing.

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