Facile Synthesis of Degradable Gels by Oxygen Cross-Linking of Polymers Including a Dienyl Group on Their Side Chain or at Chain Ends

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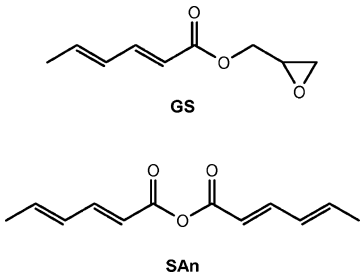
ABSTRACT: We have demonstrated a facile method for the synthesis of a new kind of degradable gel, which is prepared by the introduction of a dienyl group into the side chains or the chain ends of conventional polymers such as poly(acrylic acid), poly(ethylene oxide), poly(2-hydroxyethyl methacrylate), and poly(vinyl alcohol) and the subsequent radical copolymerization of the diene with oxygen in the presence of a radical initiator. The obtained gels contain the polyperoxy units as the cross-linking points and readily degrade upon heating. Sorbic derivatives including epoxy and anhydride functional groups are used as reagents for the dienyl functionalization of the precursor polymers with a high efficiency. The heat of degradation of the polymer gels synthesized in this study is much smaller than that of the previously reported polyperoxides as degradable polymers and gels. This method is applied to the preparation of various kinds of polymer networks programmed for degradation after temporary use.

Introduction

Chemically, physically, or topologically cross-linked polymer gels are important for industry, biotechnology, and medical applications.[1] For example, hydrogels are used as drug delivery matrices and tissue engineering scaffolds with high performance designed by a controlled network structure and combination with various kinds of polymers.[2−14] By incorporating a degradable linkage into gels, we can claim more variety of application of the gels as materials programmed for degradation after temporary use. The structural change and degradation of the network polymers are triggered by a stimulus such as heating,[1,15−19] pH,[20,21] glucose,[22] antigen,[23] and enzymatic activities.[24] We recently reported that polyperoxide (PP), as a new kind of a degradable polymer, is readily produced by the radical copolymerization of 1,3-diene monomers with oxygen under mild conditions.[25−32] The obtained PP includes a labile O−O bond in their main chain, leading to be readily degraded via a radical chain mechanism using stimuli such as heating, UV irradiation, and the addition of a base.[27,28] We also synthesized the PP gels by the radical copolymerization of bifunctional diene monomers such as ethylene glycol disorbate and vinyl sorbate with oxygen.[27] More recently, we reported the rational design of polymer gels including the PP structure as degradable junctions by the copolymerization of telechelic poly(lactic acid) (PLLA) with oxygen.[32] It was demonstrated that PLLA with a dienyl group at the α- and ω-chain ends gave PLLA gels including temporary cross-linking points, for which degradation induces a drastic change in the structure and properties of PLLA upon heating. The PLLA functionalized with a terminal dienyl group was synthesized by living anionic polymerization in our previous study. However, it is required to propose a more convenient method for the preparation of polymer networks containing a labile peroxy bond as a degradable junction for temporary cross-linking. In the present study, therefore, we introduced a dienyl group into the chain ends or the side chain of conventional polymers using reagents such as epoxy- and anhydride-containing sorbic derivatives (GS and SAn in Chart 1), and the dienyl-functionalized polymers were reacted with oxygen to yield gels containing PP units at the cross-linking points. The thermal degradation properties of the obtained gels were investigated.

Chart 1



Experimental Section

General Procedures. The number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as an eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes and poly(ethylene oxide)s. The NMR spectra were recorded using a JEOL JMN A-400 spectrometer. Differential thermal analysis (DTA) was carried out using a Seiko TG/DTA 6200 in a nitrogen stream at a heating rate of 10 °C/min. The heat of decomposition per milligram (ΔH) of the polymer was calculated from the intensity of an exothermic peak in a DTA curve and the device constant, which was determined using $AgNO_3$ and KNO_3 as the reference materials (4.43×10^6 μV·s/kJ).[26]

Materials. The solvents were used after distillation. 2,2′-Azobis-(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was recrystallized from methanol. 2-Hydroxyethyl methacrylate (HEMA) (Wako Pure Chemical Ind., Ltd. Osaka) was distilled under reduced pressure. Poly(ethylene oxide) (PEG, M_n = 910 and 600, Aldrich), poly-(acrylic acid) (PAA, $M_n = 1.5 \times 10^4$, Wako Pure Chemical Ind., Ltd. Osaka), and poly(vinyl alcohol) (PVA, $M_n = 2.52 \times 10^4$, degree of saponification = 86.5−89 mol %, Kishida Chemical Ind.,

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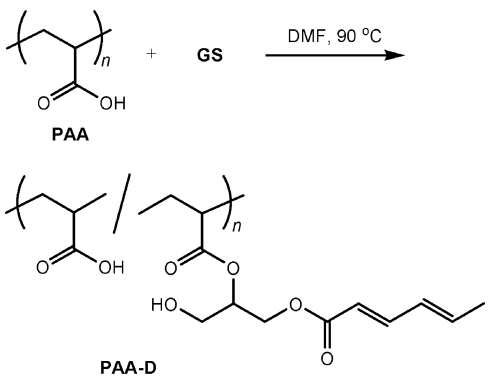
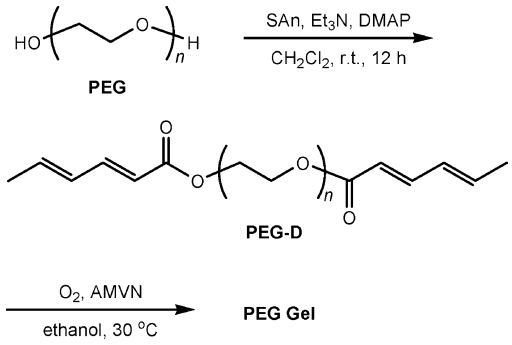
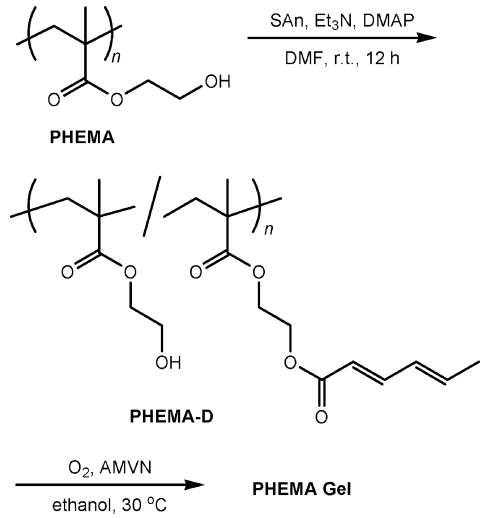
Scheme 1



Scheme 2



Scheme 3



Ltd., Osaka) were used without further purification. All other commercial chemicals were used as received without further purification.

Glycidyl Sorbate (GS). In a 50 mL three-necked flask, equipped with an efficient stirrer and a reflux condenser, was placed 16.8 g of epichlorohydrin (182.3 mmol), 10.0 g of potassium sorbate (67.0 mmol), and 0.5 g of benzyl trimethylammonium chloride (2.7 mmol). Under an argon atmosphere, the suspension was vigorously stirred and heated at 50 °C. The solution was stirred for 4 h, and the precipitation was then filtered off. The filtrate was dissolved in 50 mL of chloroform and washed three times with 80 mL of brine. After drying over Na_2SO_4, the solvent was evaporated. The pure GS was isolated by distillation under reduced pressure (bp 110 °C, 3 mmHg); yield 86.0%. The structure of the obtained GS was confirmed by ^{1}H and ^{13}C NMR spectroscopies. The spectral data for GS are as follows.

Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, J = 15.6 and 9.6 Hz, $CH_3CH{=}CHCH{=}CH$, 1H), 6.19 (m, $CH_3CH{=}CHCH{=}CH$, 2H), 5.81 (d, J = 15.6 Hz, $CH_3CH{=}CHCH{=}CH$, 1H), 4.48 and 3.99 (dd, J = 12.4 and 3.2 Hz, dd, J = 12.4 and 6.4 Hz, $COOCH_2$, 1H × 2 (geminal)), 3.25 (m, epoxy CH, 1H), 2.86 and 2.67 (dd, J = 4.8 and 4.0 Hz, dd, J = 4.8 and 2.8 Hz, epoxy CH_2, 1H × 2 (geminal)), 1.87 (CH_3, J = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.90 ($C{=}O$), 145.91 ($CH_3CH{=}CHCH{=}CH$), 140.06 ($CH_3CH{=}CHCH{=}CH$), 129.75 ($CH_3CH{=}CHCH{=}CH$), 118.10 ($CH_3CH{=}CHCH{=}CH$), 64.79 ($COOCH_2$), 49.53 (epoxy CH), 44.72 (epoxy CH_2), 18.69 (CH_3).

Sorbic Anhydride (SAn). In a 100 mL round-bottom flask, equipped with a magnetic stirrer and a dropping funnel, was placed 11.2 g (0.10 mol) of sorbic acid and 14 mL (0.10 mol) of triethylamine in 40 mL of dichloromethane. The solution was cooled in an ice−water bath, and 13.43 g (0.05 mol) of diphenyl phosphorochloridate (Wako Pure Chemical Ind., Ltd., Osaka) in 10 mL of dichloromethane was dropwise added over 30 min with stirring. After the addition, the reaction mixture was further stirred at room temperature for 3 h. The solution was filtered off and washed three times with 30 mL of cold brine. The organic layer was filtered through a glass filter charged with sufficient silica gel (ca. 15 g) to decolorize the solution and remove the residual acid. After evaporating the solvents, the resulting white solid was recrystallized from cold *n*-hexane. SAn was obtained as a white precipitate in a 7.14 g yield (70.0%).

Needles; mp 36−38 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, J = 15.6 and 10.4 Hz, $CH_3CH{=}CHCH{=}CH$, 1H), 6.26 (m, $CH_3CH{=}CHCH{=}CH$, 2H), 5.85 (d, J = 15.6 Hz, $CH_3CH{=}CHCH{=}CH$, 1H), 1.90 (s, J = 4.8 Hz, CH_3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.96 ($C{=}O$), 148.86 ($CH_3CH{=}CHCH{=}CH$), 142.41 ($CH_3CH{=}CHCH{=}CH$), 129.73 ($CH_3CH{=}CHCH{=}CH$), 117.73 ($CH_3CH{=}CHCH{=}CH$), 18.94 (CH_3).

Polymerization of HEMA. HEMA in ethanol (2 mol/L, 30 mL) was added to a dried Schlenk flask, equipped with a stirring bar. After sealing it with a rubber septum, the solution was frozen in a dry ice−methanol bath and degassed by three freeze−pump−thaw cycles. AMVN (HEMA/AMVN = 100/1 by weight), as an initiator, was introduced, and the vial was degassed, backfilled with argon, and stirred at 30 °C in a thermostated oil bath for 12 h. The flask was then removed from the oil bath, and the solution was poured into a large amount of diethyl ether to precipitate poly(HEMA) (PHEMA). The isolated PHEMA was reprecipitated using ethanol and diethyl ether and dried in vacuo overnight at room temperature. The isolated polymer yield was gravimetrically determined. Yield 56.5%. The acetylation of PHEMA using excess acetic anhydride yields a THF-soluble polymer, which was provided for evaluating the molecular weight by GPC. The M_n of the acetylated PHEMA was 5.8 × 10^4.

Polymer Reactions. The reaction of PAA with GS was carried out in a sealed glass tube. After the required amounts of PAA, GS, and *N*,*N*-dimethylformamide (DMF) were charged, the tube was degassed and then sealed under high vacuum. After the reaction at 90 °C for a given time, the solution in the tube was poured into a large amount of diethyl ether to precipitate the product polymer. The isolated polymer was reprecipitated with ethanol and diethyl ether and dried in vacuo overnight at room temperature.

The reaction of PEG with SAn was carried out as follows. In a 100 mL round-bottom flask, equipped with a magnetic stirrer and a dropping funnel, was placed the required amount of PEG, triethylamine, and 4-(dimethylamino)pyridine (DMAP) in 20 mL of dichloromethane. The reaction of PHEMA and PVA was performed using dimethyl sulfoxide (DMSO) as the solvent. The polymer solution was cooled in an ice−water bath, and the required amount of SAn was slowly added with stirring. After addition, the reaction mixture was further stirred at room temperature overnight. The reaction mixture was poured into a large amount of diethyl ether to precipitate the product polymer, and the isolated polymer

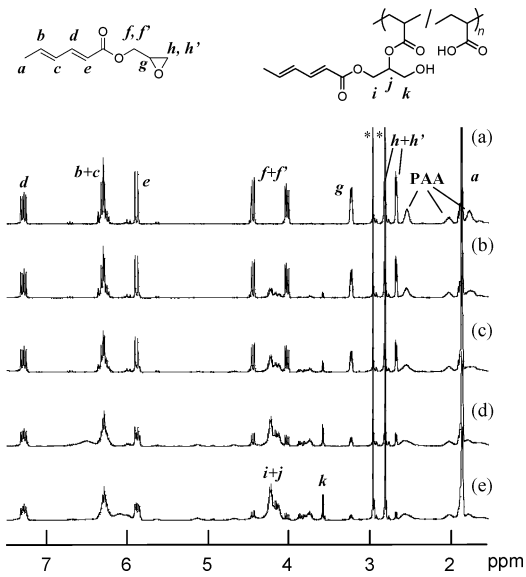


Figure 1. Change in the ^{1}H NMR spectrum of the mixture of GS and PAA in DMF-d_7 heated at 90 °C for (a) 0, (b) 2, (c) 4, (d) 10, and (e) 16 h. [GS]/[COOH] = 1/1 in feed. An asterisk indicates peaks due to the solvent.

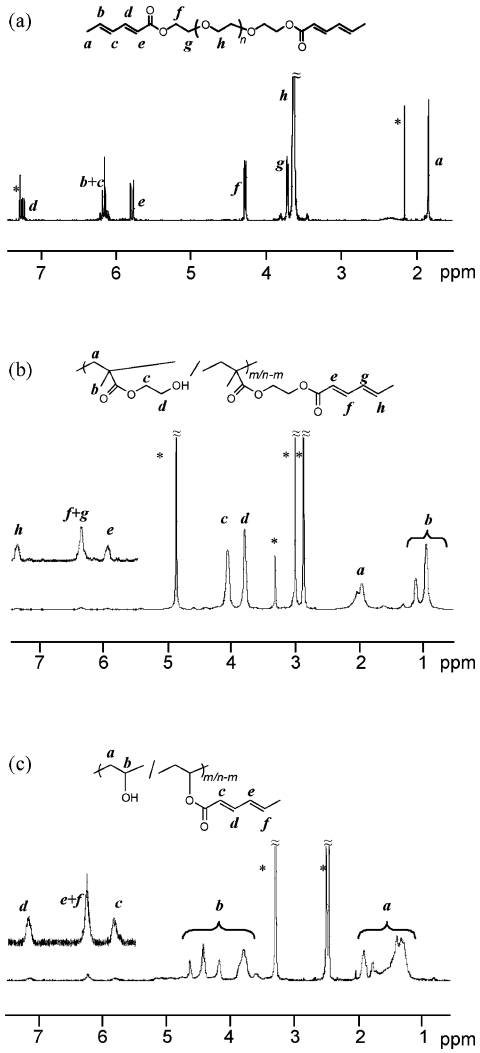


Figure 2. ^{1}H NMR spectra of dienyl-functionalized polymers: (a) PEG-D in $CDCl_3$ (run 4), (b) PHEMA-D in CD_3OD (run 5), (c) PVA-D in DMSO-d_6 (run 7). An asterisk indicates peaks due to solvents.

was reprecipitated again and dried in vacuo overnight at room temperature.

All the dienyl-functionalized polymers (PEG-D, PAA-D, PHEMA-D, and PVA-D) were kept under argon atmosphere or in vacuo in the dark in order to prevent autooxidation.

Oxygen Cross-Linking. Dienyl-functionalized polymer (typically 0.5 g), AMVN as the radical initiator (polymer/AMVN = 50/1 by weight), and ethanol or DMSO (PEG/ethanol = 1/2, PAA/ethanol = 1/5, PHEMA/ethanol = 1/5, and PVA/DMSO = 1/10 by weight) were charged into an unsealed Pyrex tube. The radical copolymerization of the dienyl groups in the polymers with oxygen was carried out with bubbling oxygen into the solution at 30 °C. After the reaction, the mixture was poured into a large amount of diethyl ether to precipitate the polymers, which were filtered, washed, and then dried in vacuo overnight at room temperature. The dried polymer was poured into a large amount of ethanol or DMSO and divided into insoluble and soluble parts. The gel isolated as the insoluble part was dried in vacuo at room temperature. The gel fraction ratio was determined gravimetrically. The polymer was soaked in a solvent at room temperature for 5 h, and the degree of swelling was determined as the relative ratio of the swollen gel to the dried gel in weight.

Results and Discussion

PAA Gel. An epoxy compound undergoes a ring-opening reaction with a variety of reagents such as amines, alcohols, carboxylic acids, and anhydrides. Because polymers including a carboxylic acid in the side chain are expected to react with an epoxide to readily form an ester, we used GS for the introduction of a dienyl group into PAA (Scheme 1).

In the IR spectra of the polymer isolated after the reaction, the characteristic peaks due to the stretching of a conjugated double bond around 1650 cm^{-1} as well as the C−O bond in the ester group at 1330 cm^{-1} were detected. The absorption intensity decreased for the peak due to the C−O−H bending of the carboxyl group at 1415 cm^{-1} according to the process of the reaction. When we monitored the reaction of PAA with GS in DMF-d_7 at 90 °C by ^{1}H NMR spectroscopy (Figure 1), signals assigned to the structure of GS incorporated into PAA (peaks *i*, *j*, and *k*) were detected. When an epoxy ring is reacted with carboxylic acid, the position for the cleavage of the covalent bond depends on the reaction conditions, acidic or alkaline, and the kind of catalyst. In the present study, we carried out the reaction in DMF in the absence of a catalyst. The NMR results suggest that the product is formed according to an acidic ring-opening mechanism.

The degree of the introduction of a dienyl group into PAA increased with an increase in the reaction time and reached a constant value after a 10 h reaction. The conversion of the carboxylic acid to the ester was 56%, and the quantitative transformation of carboxylic acid into the ester was difficult under the conditions used in this experiment ([GS]/[COOH] = 1, no catalyst). Table 1 summarizes the results for the reaction of PAA with a different amount of GS in the feed ([GS]/[COOH] = 0.05−0.20). The amount of the introduced dienyl group depended on the ratio of [GS]/[COOH] in the feed; i.e., the dienyl group was incorporated into the side chain during 2.0−12.2% conversion. As a result, half of the amount of the used GS was incorporated into the polymer irrespective of the [GS]/[COOH] ratio.

When we carried out oxygen cross-linking of the obtained dienyl-functionalized PAA (PAA-D), the gel was obtained in a 34−78% yield (Table 1). The isolated PAA gel swelled with water, methanol, and ethanol. The degree of swelling depended on the cross-linking density of the gels. When the GS concentration in the feed increased for the preparation of PAA-D, the degree of swelling of the obtained gel decreased.

The copolymerization of GS with oxygen gave PP−GS, similar to the other PP products previously reported.[25,26]

Table 1. Reaction of PAA with GS and Oxygen Cross-Linking of Obtained PAA-D[a]

run	[GS]/[COOH] in feed	dienyl group in PAA-D (%)	gel yield after oxygen cross-linking (wt %)	degree of swelling of gel (%)		
				water	methanol	ethanol
1	0.05	2.0	34.1	510	750	500
2	0.10	4.8	77.9	530	630	340
3	0.20	12.2	65.8	160	250	210

[a] The reaction of PAA with **GS** was carried out in DMF at 90 °C for 12 h. The amount of the introduced dienyl group was determined by ^{1}H NMR spectroscopy. The oxygen cross-linking of PAA-D was carried out with bubbling oxygen in the presence of AMVN in ethanol at 30 °C for 12 h.

Table 2. Reaction of PEG, PHEMA, and PVA with SAn and Oxygen Cross-Linking of Obtained Dienyl-Functionalized Polymers

run	polymer	solvent	[SAn]/[OH] in feed	introduced dienyl group (%)	gel yield (%)	degree of swelling of gel (%)		
						water	methanol	DMSO
4	PEG[a]	CH_2Cl_2	1.5	7.9[b]	48.8	560	210	590
5	PHEMA	DMF	0.1	8.6	70.9	*c*	260	510
6	PHEMA	DMF	0.2	19.0	84.0	*c*	250	350
7	PVA	DMSO	0.1	6.4	45.7	160	190	480
8	PVA	DMSO	0.2	13.6	57.8	*c*	110	260

[a] $M_n = 910$. [b] The ratio of the number of the introduced dienyl groups relative to the number of repeating unit. The functionality of the polymer chain ends was 0.98. [c] No swelling.

However, the epoxy group in the side chain of PP−GS was difficult to be reacted with di- or multifunctional compounds in order to obtain a gel without any degradation of the main chain of the PP−GS consisting of thermally unstable peroxy bonds.

PEG, PHEMA, and PVA Gels. Hydroxy-containing polymers such as PEG, PHEMA, and PVA readily react with a carboxylic anhydride compound to give an ester as the product under mild reaction conditions. In the present study, we used SAn as another reagent for the introduction of the dienyl group into the polymers. First, PEG with a hydroxy group in both chain ends was reacted with an excess of SAn (1.5 equiv relative to the hydroxy group of PEG) in the presence of DMAP and triethylamine as a base catalyst for the esterification at room temperature for 12 h. The resulting PEG with terminal diene moieties (PEG-D) gives the cross-linked PEG (PEG gel) with peroxy junctions when it is reacted with oxygen, as shown in Scheme 2.

Figure 2a shows the ^{1}H NMR spectrum of PEG-D. In addition to the signals of the methylene protons of the original PEG at 3.65 ppm, we can see characteristic peaks assigned to the methyl protons at 1.8 ppm, the methylene protons due to the terminal repeating unit of PEG at 4.37 ppm, and the protons due to the dienyl groups observed at 5.8, 6.2, and 7.2 ppm. From the integrated peak intensities, PEG-D includes dienyl groups at both chain ends with a high efficiency ($f = 0.98$). The M_n value of PEG-D was determined to be 1100 by GPC analysis. This value agrees well with the sum of the molecular weights for the original PEG ($M_n = 910$) and two sorbic groups at the polymer chain ends. We further carried out the reaction of PEG-D with oxygen to obtain a cross-linked polymer. The chloroform-insoluble fraction was 48.8 wt %. The PEG gel swelled with DMSO, chloroform, THF, methanol, and water.

PHEMA was reacted with GS in DMF similarly as shown in Scheme 3. Figure 2b shows the ^{1}H NMR spectrum of the dienyl-functionalized PHEMA (PHEMA-D). The efficiency of the introduction of the dienyl group was 8.6 and 19.0% when the [SAn]/[OH] ratio was 0.1 and 0.2, respectively (Table 2). Commercially available PVA was also used for the reaction with SAn (Scheme 4). The ^{1}H NMR spectrum of the functionalized PVA (PVA-D) in Figure 2c evidences the process of the reaction for the introduction of dienyl groups into the side chain.

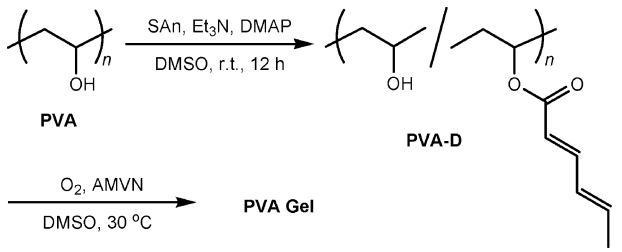
The results for the reaction of the dienyl-functionalized polymers with oxygen are summarized in Table 2. The results indicate that the obtained yield of the gels increased as the fraction of the amount of the dienyl group introduced in the polymer, irrespective of the structure of the polymers and the position of the introduced dienyl groups, i.e., a side chain or a chain end.

Table 3. Radical Copolymerization of SAn and MS in the Presence of Oxygen[a]

run	[SAn]/[MS] in feed (mol/mol)	polymer yield (%)	gel fraction[b] (%)
9	1/9	40.7	37.7
10	2/8	52.2	65.2

[a] Copolymerization was carried out with bubbling oxygen at 30 °C in the presence of AMVN in 1,2-dichloroethane for 6 h. Monomer/solvent = 1/1 by weight. Monomer/AMVN = 50/1 by weight. [b] The chloroform-insoluble part of the obtained polymer.

Scheme 4



SAn Gel. The copolymerization of SAn and methyl sorbate (MS) in the presence of oxygen was carried out to obtain a PP gel, which has a polymer structure different from the degradable gels described above. The resulting PP(SAn-*co*-MS) includes a reactive anhydride group as the bridge for cross-linking or the dangling side chain (Scheme 5). Actually, as shown in Table 3, the PP(SAn-*co*-MS) gel was obtained as the chloroform-insoluble part. The amount of the isolated gel fraction increased with an increase in the SAn concentration in the feed as expected.

We further examined a polymer reaction using the resulting PP(SAn-*co*-MS) gel with methanol or PEG ($M_n = 600$) in THF at room temperature for 24 h in the absence of a base catalyst (Table 4) because DMAP cannot be used in this case due to the degradation of PP by basic compounds. A change in the solubility of the gel after the reaction with methanol indicates the quantitative cleavage of anhydride linkages by methanolysis to yield PP−MS. In the ^{1}H NMR spectrum of the obtained

Table 4. Reaction of PP(SAn-*co*-MS) Gel with Hydroxy Compounds under Various Conditions[a]

run	reactant	weight (g)	THF (mL)	solubility after reaction
11	none[b]	0	5.0	insoluble
12	methanol	3.95	5.0	soluble
13	PEG[c]	2.00	5.0	soluble
14	PEG[c]	0.40	2.5	partly soluble
15	PEG[c]	0.08	8.0	insoluble

[a] The reaction was carried out using 0.1 g of PP(SAn-*co*-MS) gel (run 10) for 24 h at room temperature. [b] Control experiment. [c] $M_n = 600$.

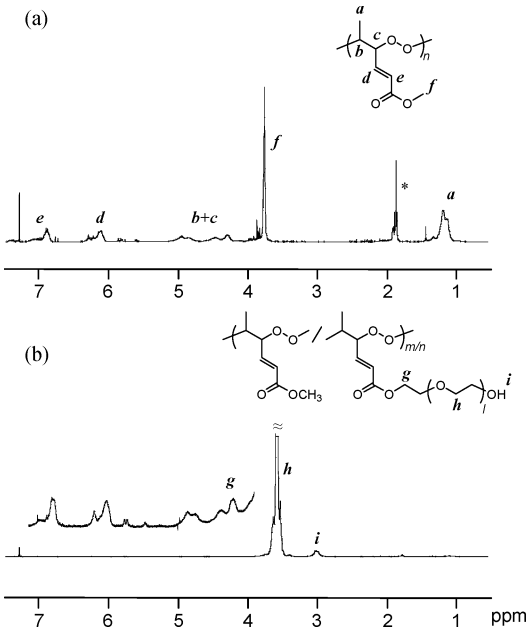


Figure 3. ^{1}H NMR spectra of (a) the polymer obtained by the reaction of the PP(SAn-*co*-MS) gel with methanol (run 12) and (b) the polymer obtained by the reaction of the PP(SAn-*co*-MS) gel with PEG (run 13). An asterisk indicates peaks due to solvents.

polymer after the reaction with methanol (Figure 3a), the characteristic peaks due to the vinylene protons in the side chain were observed at 6.1 and 6.9 ppm (*d* and *e*) as well as the splitting peaks at 4−5 ppm due to the methine protons in the main chain (*b* and *c*). This spectrum is similar to that of PP prepared by the copolymerization of MS with oxygen (PP−MS) previously reported.[25] The fact that no peak due to the unreacted dienyl group of the SAn unit was detected in the spectrum suggests the quantitative transformation from the anhydride group as the cross-linker of the gel to the methyl esters. The M_n and M_w/M_n values of the solubilized PP were 2.4×10^3 and 3.2, respectively. These values were also similar to those for the previously reported PP.[25−28] This result supports the absence of degradation of PP(SAn-*co*-MS) during the transesterification.

The reaction of PP(SAn-*co*-MS) with PEG was also carried out. With a decrease in the amount of the used PEG, the gel was partly soluble or insoluble after the reaction, as shown in Table 4 (runs 14 and 15). The polymer mixture was divided into insoluble and soluble fractions by solvent extraction. The insoluble polymer included the PEG units as the pendant group in the polymer chain as well as the linkage unit of the cross-linked polymer gels. In this case, the reaction with the hydroxyl-terminated PEG results in the formation of an alternate cross-linking structure. In the ^{1}H NMR spectrum of the soluble polymer, which was prepared by the reaction with a large amount of PEG (run 13), the signal of the methylene protons

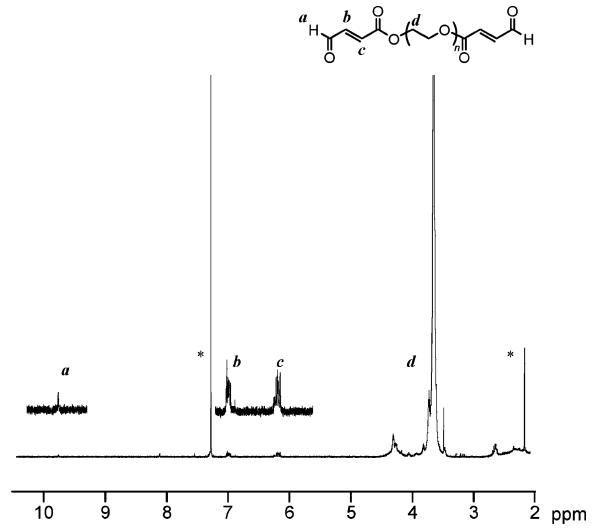


Figure 4. ^{1}H NMR spectrum of the linear PEG as the product during the thermal degradation of the PEG gel in toluene at 90 °C for 3 h. Asterisks indicate peaks due to solvents.

Table 5. Heat of Degradation for Various Polymers Including PP Structure as the Cross-Linking Points or Repeating Units

run	polymer	introduced dienyl group (%)	ΔH (J/g)
16	PAA gel	2.0	5.2
17	PEG gel	7.9	7.4
18	PHEMA gel	8.6	16.9
19	PHEMA gel	19.0	55.5
20	PP−MS (linear polymer)		474.0
21	PP−(MS-*co*-EDS) gel[a]		440.2

[a] [MS]/[EDS] = 7/3 in the feed for the polymerization.

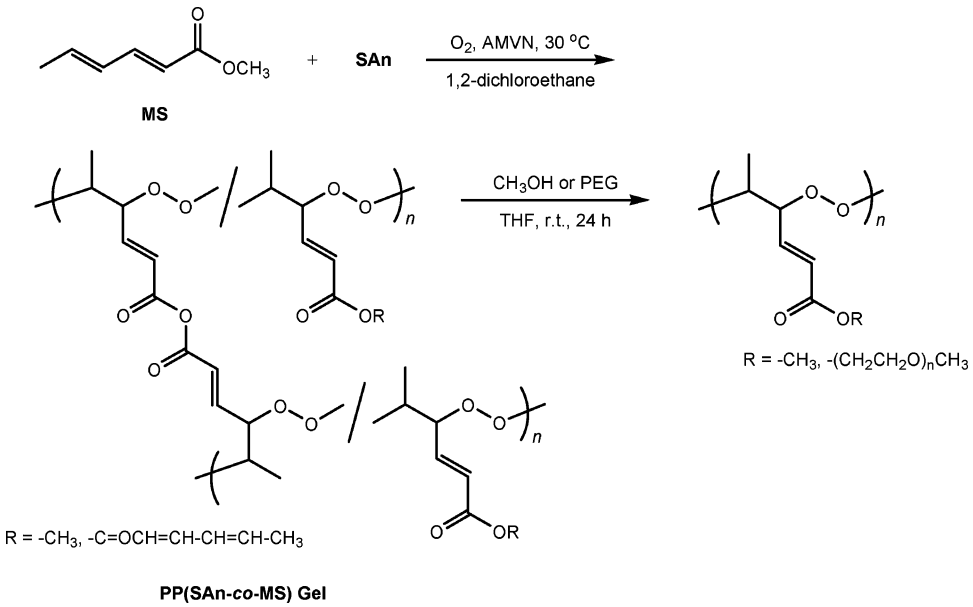
around 4.2 ppm due to the methylene unit of the PEG side chain adjacent to the ester group was detected (Figure 3b).

Degradation Reaction. We investigated the photodegradation and thermal degradation behavior of the PEG gel. The PEG gel swollen with water became partly soluble after a 3 h irradiation of UV light due to the dissociation of the peroxy linkage as expected. However, some insoluble fraction (19%) remained even after 15 h irradiation. The molecular weight of the soluble polymer was twice that of the original PEG (M_n = 1910 after the reaction). The photoirradiation through Pyrex ($h\nu$ > 280 nm) may result in the slow degradation of the peroxy linkages. The thermal degradation of the gel was also examined. As a result, the PEG gel swollen with toluene became entirely soluble upon heating at 110 °C for 3 h in a sealed tube. The M_n value of the PEG recovered by reprecipitation was 1360, similar to that of the original PEG (M_n = 1100).

The peroxy linkage as the junction of the cross-linking of the gels is cleft on heating to produce oxygen-centered radicals at the first step of the degradation. They further undergo β-scission to give an aldehyde-terminated PEG and acetaldehyde as the volatile component. The terminal structure of the polymer after thermal degradation was examined by ^{1}H NMR spectroscopy (Figure 4). The characteristic peaks due to an aldehyde proton at 9.7 ppm and vinylene protons at 6−7 ppm were detected. These results strongly indicate that a peroxy linkage as the cross-linking point in PEG gel readily degrades according to a mechanism the same as the previously reported one.[25,26]

The degradation of PAA swollen with ethylene glycol upon heating at 140 °C for 0.5 h yielded a clear and homogeneous solution. When the degree of cross-linking of the gels increased, the degradation behavior became more complex, and the residue

Scheme 5



insoluble in solvents remained after the degradation. Any undesirable reaction such as a combination of the generating radicals and an addition to the residual dienyl group might occur in the polymer network. To completely degrade the gel upon heating, the degree of the introduction of dienyl groups into the polymers is better at less than a few percent. The small amount of the introduced dienyl groups, i.e., the peroxy linkage derived from them, has another merit for the reduction of the heat of degradation when the polymers are used for application.

In this study, the DTA measurement of the dried gels was carried out to evaluate the heat of degradation. In the DTA curves, an exothermic peak due to the degradation of peroxy linkages was observed. The results of the estimation of the heat of degradation of the polymer gels are summarized in Table 5. The heats of degradation of the polymer gels cross-linked by peroxy bonds (runs 16−19) are $10-10^2$ times smaller than that of PP obtained by the copolymerization of MS and ethylene glycol disorbate (EDS) with oxygen (runs 20 and 21). PAA, PEG, and PHEMA gels include small amounts of the PP units as the junctions for cross-linking, while PP−MS and PP−MS/EDS consist of successive PP repeating units in their main chain. Such a reduced exothermic value during the degradation is advantageous for use as degradable gels of conventional polymers. The suppressed amount of the introduced dienyl group is preferred for a decrease in the heat of degradation and complete degradation without side reactions, yielding an insoluble residue.

Conclusions

We have demonstrated a facile method for the introduction of dienyl groups into conventional polymers including carboxy and hydroxy groups in the side chain or chain ends. The introduction of dienyl groups into PAA using GS proceeded without any catalyst at 90 °C, and the degree of the introduction was controlled by the reaction time and the molar ratio of GS relative to the carboxy groups of PAA in the feed. SAn was also allowed to react with hydroxy-containing polymers such as PEG, PHEMA, and PVA to yield the dienyl-functionalized polymers. The reaction effectively occurred in the presence of DMAP and triethylamine as the catalyst. Especially, in the case of PEG, the hydroxy group was quantitatively converted into the dienyl ester group. The subsequent radical copolymerization of the dienyl-functionalized polymers with oxygen gave gels containing the peroxy linkage as the cross-linking points. The obtained gels readily degraded upon heating and became soluble in a solvent. The heat of degradation of the polymer gels derived from conventional linear polymers in this study is much smaller than that of the previously reported PP polymers and gels. Thus, an oxygen cross-linking method using the dienyl-functionalized polymers derived from conventional polymers has prospects for an application to provide the polymeric materials with a degradable junction as temporary cross-linking.

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