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Production of oil-based binder by RAFT polymerization technique

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ABSTRACT

In this study, air-blown linseed oil was styrenated by reversible addition–fragmentation chain transfer polymerization (RAFT). For this purpose, hydroperoxide groups were formed in the structure of linseed oil by blowing air through it. The oxidized oil was used as a macroinitiator in the styrenation process by RAFT technique using phenacyl morpholine dithiocarbamate (PMDC) as a RAFT agent. The obtained samples were characterized by GPC and FT-IR measurements. The effects of various parameters, such as the amount of PMDC, the number of peroxide groups, and the reaction time were investigated on polydispersity and molecular weight. For comparison, a copolymer sample was also prepared in the absence of PMDC. The film properties of all the samples were determined according to the related standards and compared. The sample obtained by the RAFT technique exhibited better film properties and a relatively narrow polydispersity, showing that the RAFT technique provides good control over the polymerization system in this study.

1. Introduction

Triglyceride oils have had a pivotal value as an ingredient for decorative and protective organic coating formulations for years because they can polymerize and cross-link or dry after they have been applied to a surface to form tough, adherent films. Drying oils can be modified in simple ways, such as thermal polymerization and air blowing. For better film performance, oils are subjected to copolymerization with vinyl monomers, most frequently with styrene [1]. However, in classical styrenation, homopolystyrene formation leading to weak film properties is likely to occur. In order to eliminate this disadvantage, various studies have been carried out by our group [2–9]. The strategy in these studies was to obtain macromonomer by inserting vinyl groups into the oil structure or by preparing a macroinitiator having a large oil moiety. In our very recent study, nitroxide-mediated radical polymerization (NMRP) was applied to the styrenation process of triglyceride oil. By applying this controlled/living radical polymerization (CLRP), styrenated oil samples with narrow polydispersity and controlled structure could be obtained [10]. In the NMRP method, 2,2′,6,6′-tetramethylpiperidinyl-1-oxy (TEMPO) was used as a reversible terminating agent. Due to the stability of the TEMPO radical, polymer growth takes place in a controlled manner, in which monomer is added to the polymer radical between successive activation and deactivation reactions [11,12].

In continuation of those previous studies, in the present study the reversible addition–fragmentation chain transfer (RAFT) polymerization technique was applied to the styrenation of the triglyceride oils. It is well known that, in the RAFT polymerization, thermally generated free radicals start to grow, and when they encounter the RAFT agent, a reversible addition take places between these radicals and the RAFT agent [13,14]. This polymerization mechanism is different from that of NMRP, as mentioned above. For this reason, it is worthwhile to investigate and compare the effects of the techniques, NMRP and RAFT, on the polymer structure and properties.

The goal of this study is to apply the RAFT technique to obtain the styrenated oil. For this, air-blown linseed oil was prepared and used as a macroinitiator in the styrenation of triglyceride oil by the RAFT polymerization method in the presence of phenacyl morpholine dithiocarbamate (PMDC). The effects on the polydispersity of the amount of PMDC, the peroxide content, and reaction time were investigated. In parallel experiments, the polymerization process was carried out without using PMDC under the same experimental conditions. The film properties of the obtained products were determined according to the related standards and compared with each other. At the end of these studies, it was understood that the sample obtained by RAFT polymerization has a low polydispersity index and also good film properties.

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2. Experimental

2.1. Materials

Commercially purchased linseed oil was used as the oil component. Styrene (St, 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor. Methanol was obtained from Aldrich Chemical Co., Ltd., and used as received. Carbon disulfide (99.5%, Merck) was used as received. Morpholine (99%, Merck) was stored over sodium metal under nitrogen atmosphere for 24 h and distilled before use. Other solvents purified by conventional procedures.

2.2. Characterization

The molecular weight and polydispersity of polymers were determined by gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran as the eluent at a flow rate of 0.3 ml min^{-1}. Molecular weights were determined using polystyrene standards.

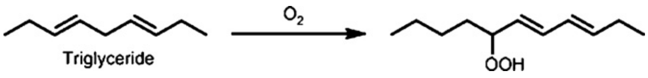
The Fourier-Transform infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer.

2.3. Preparation of air-blown linseed oil

Air was passed through pre-heated linseed oil with a flow rate of 2 L min^{-1} for 3 and 18 h at 80 °C in a temperature-controlled system. The peroxide values of air-blown linseed oils thus obtained were then determined according to the literature [15].

2.4. Synthesis of phenacyl morpholine dithiocarbamate (PMDC)

This compound was prepared in 68.8% yield, according to the method as described in [16]. mp: 129.5 °C. UV (CH_2Cl_2): λ_{max}: 300 nm (ε: 4882 mol^{-1} L cm^{-1}); FT-IR (ATR): 3055, 2920, 2830, 1702, 1470, 1390, 1310, 1280, 1140, 1065, 860, 820, 790, 690 cm^{-1}.



Scheme 1. The formation of hydroperoxide groups in the oil's structure.

^{1}H NMR (250 MHz, $CDCl_3$, ppm): 7.8 aromatic; 5.0 C–CH_2–S; 3.8–4.4 CH_2.

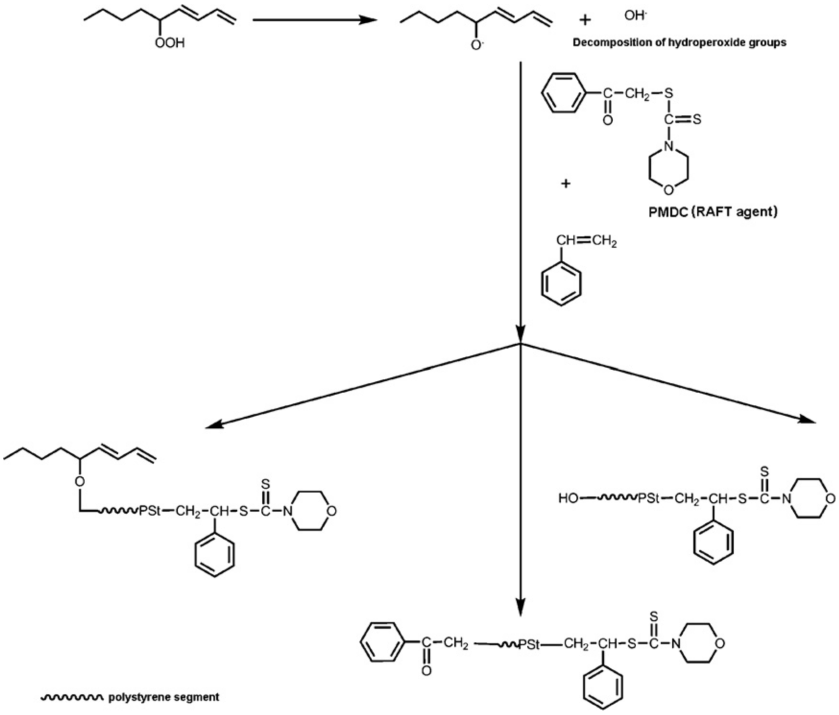
^{13}C NMR (62.5 MHz, $CDCl_3$, ppm): 44.8, 46.9, 47.3, 50.1, 51.3, 66.2 CH_2; 128.5, 128.7, 133.5, 136.1 aromatic; 193.0 C=O; 195.9 C=S.

2.5. Styrenation of air-blown linseed oil in the presence of PMDC

A given amount of PMDC as a RAFT agent (varied equivalents with respect to the peroxide number) was dissolved in 1,4-dioxane and then added to the flask containing the air-blown linseed oil (1.0 g, 7.2×10^{-4} mol) and styrene (1.0 g, 9.6×10^{-3} mol). The mixture was then purged with nitrogen for 10 min to eliminate oxygen. The vessel was then immersed in an oil bath preheated to 90 °C. After the required duration, the reaction was quenched by cooling the flask. The polymer product was precipitated in methanol, washed with methanol, and dried under vacuum at 30 °C for 24 h. The polymerizations yields were estimated gravimetrically.

2.6. Determination of film properties

Film properties such as drying time [17], flexibility [18], adhesion [19], hardness [20], water resistance [21], alkali resistance [21], and acid resistance [21] were determined. For this purpose, each sample was thinned with xylene to 30% solid content, and 0.5% lead naphthenate and 0.05% cobalt naphthenate as metal based on solid content were added. Driers were added 24 h before the film application. To determine the drying time and hardness, films of polymers (40 μm) were prepared on glass surfaces by using an automatic film applicator. In the flexibility, water resistance, and adhesion tests, tin plate panels were used as a substrate. For the other tests (alkali



Scheme 2. The overall process of styrenation of air-blown linseed oil in the presence of PMDC.

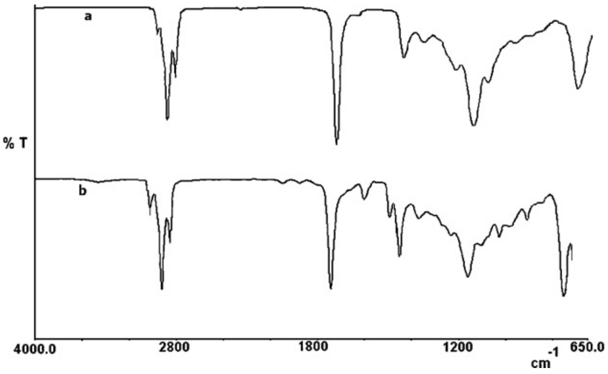


Fig. 1. FT-IR spectra of air-blown linseed oil (a) and styrenated oil sample obtained at 90 °C in the presence of PMDC in equivalent amounts to the generated radicals (b).

and acid resistance), a dipping method was employed, and glass tubes were used, as explained in the related standard methods.

3. Results and discussion

Air blowing is one of the well-known routes for changing an oil's structure. As shown in Scheme 1, the hydroperoxide groups are created in the oil's structure. These groups serve as an initiator for the free radical polymerization of oils [1,10]. Because no additional compound except air is used, the process is not complicated, and no further purification step is required.

Taking this fact into consideration, in this study, hydroperoxide groups were formed by blowing air through the linseed oil with a flow rate of 2 L min^{-1} for 18 h at 80 °C (Scheme 1), resulting in an oil with a peroxide value of 485 meq peroxide-oxygen/kg oil [15]. This oxidized oil was used as a macroinitiator in the styrenation step by the RAFT technique in the presence of PMDC. The overall process is summarized in Scheme 2.

The structures of the styrenated oil samples thus obtained were characterized by means of FT-IR and GPC analyses. The polymer samples used in these analyses were based on the air-blown oil with a peroxide value of 485 meq peroxide-oxygen/kg oil and the amount of PMDC was equivalent to the peroxide groups. FT-IR spectrum of the sample showed the characteristic bands of both the styrene and ester groups of the oil portion at 1600 and 1750 cm^{-1}, respectively (Fig. 1).

The GPC curves of the original and air-blown linseed oils are given in Fig. 2. Additionally, GPC curves of the styrenated oils prepared for different reaction times using the RAFT technique are shown in Fig. 3. As shown in these figures, although the original linseed oil gives a unimodel curve, the GPC curves of the air-blown linseed oil and styrenated oil, prepared for different reaction times, demonstrate three shoulders. Similar results were also obtained in our previous study [10], in which styrenated oil was prepared by NMRP technique starting with air-blown linseed oil.

As shown in the reaction mechanism (Scheme 2), upon thermal decomposition of the hydroperoxide groups, both oil-derived and hydroxyl radicals are formed concomitantly. Because the fatty acids are randomly distributed among the triglyceride molecules, hydroperoxide functionality is not the same for each air-blown oil molecule, and as a result, oil-derived radicals are not distributed evenly in the oil structure. These unevenly distributed reaction sites, together with the hydroxyl radicals with very low molecular weight cause the deviation from the unimodel shape in the GPC curves of the styrenated oil samples.

Additionally, during the blowing process, decomposition of the hydroperoxide groups might occur to some extent and cause the molecules to grow by combination and abstraction reactions, yielding a blown oil having molecules with different molecular weights. By this reasoning, shoulders are likely to occur on the GPC curves of blown oil as well.

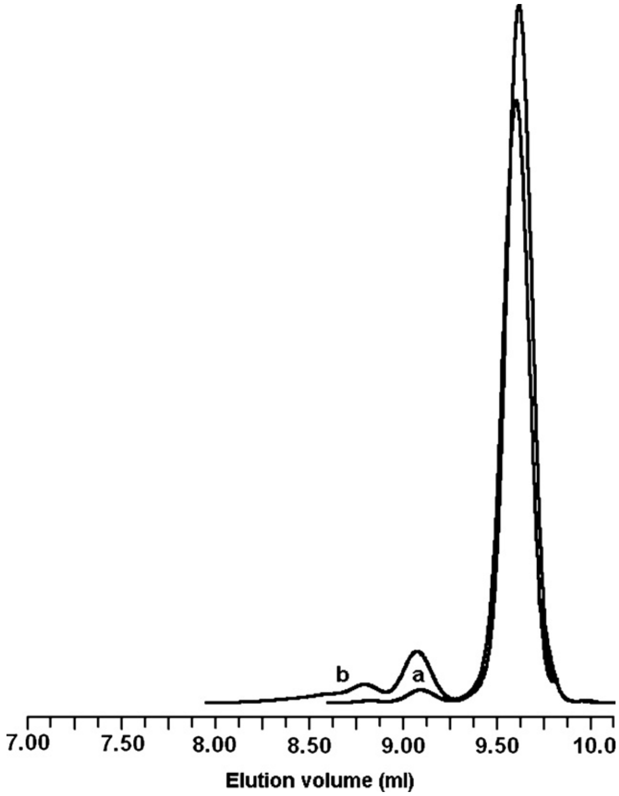


Fig. 2. GPC curves of the original linseed oil (a) and air-blown linseed oil (b).

In order to understand the effect of peroxide content on the polydispersity, the samples were prepared starting with blown oil samples with lower and higher peroxide content. As shown in Table 1, even in the case of a higher peroxide content, a lower polydispersity could be obtained.

In order to investigate the effect of the amount of PMDC, a series of polymerizations was carried out using various [peroxide]/[PMDC] molar ratios under the same experimental conditions. The results of these experiments are summarized in Table 2.

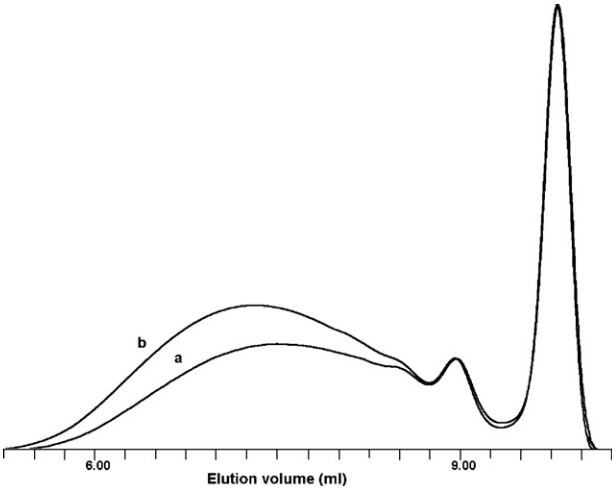


Fig. 3. GPC curves of a sample obtained in the presence of PMDC in an equivalent amount to the radicals at 90 °C for 24 h (a), 72 h (b).

Table 1
Molecular weights and polydispersities of the styrenated oil samples obtained from air-blown linseed oil with different peroxide values in the presence of PMDC.

Sample code	Peroxide number (meq peroxide-oxygen/kg oil)	[Peroxide]/[PMDC] (mol/mol)	Time (h)	Conversion[a] (%)	Molecular weight[b] (M_n)	M_w/M_n
BO-RAFT2-LP	163	1/2	24	30.12	5690	1.33
BO-RAFT2-HP	485	1/2	24	39.28	6648	1.3

[a] Conversion of styrene was determined gravimetrically.
[b] Estimated by GPC based on polystyrene standards.

Table 2
The effect of the amount of PMDC on molecular weight and polydispersity at 90 °C for 24 h.[c]

Sample code	[Peroxide]/[PMDC] (mol/mol)	Conversion[a] (%)	Molecular weight[b] (M_n)	M_w/M_n
BO-RAFT0	–	70.2	10,484	2.37
BO-RAFT1	1/1	59.36	6639	1.71
BO-RAFT2	1/2	39.28	6648	1.3
BO-RAFT3	1/3	37.2	5006	1.26

[a] Conversion of styrene was determined gravimetrically.
[b] Estimated by GPC based on polystyrene standards.
[c] The blown oil with a peroxide value of 485 meq peroxide-oxygen/kg oil was used in these experiments.

Table 3
The change of molecular weight and polydispersity of styrenated oil samples obtained in the presence of PMDC in different reaction times at 90 °C.

Sample code	Time (h)	Conversion[a] (%)	Molecular weight[b] (M_n)	M_w/M_n
BO-RAFT2	24	39.28	6648	1.3
BO-RAFT2	72	68.6	8017	1.5

[a] Conversion of styrene was determined gravimetrically.
[b] Estimated by GPC based on polystyrene standards.

As shown, in order to obtain a polydispersity lower than 1.5, the amount of RAFT agent must be used at least in an equivalent amount to the free radicals. However, if the RAFT agent was used in a higher amount than the equivalent, the polydispersity was forced to decrease to some extent. The higher [RAFT agent]/[initiator] ratio provides better control over the molecular weight through addition–fragmentation reactions [22].

In addition to these findings, when the reaction time increased, while polymer with higher molecular weight and higher conversion was obtained, polydispersity was still at a low level (Table 3).

In order to determine the performance of the obtained samples as an oil-based binder, their films were tested according to the related standards, and the results are shown in Table 4.

As shown, the samples prepared in the presence of PMDC showed better drying time, flexibility, adhesion, and water and alkali resistance, while the BO-RAFT0 sample had relatively poor film properties. Because oil in the polymer structure served as a plasticizer, chemically attaching oil moieties to the polystyrene segments increased the flexibility and adhesion of film samples. In conclusion, it should be stated that the styrenated oils obtained by the RAFT polymerization technique can be used as an oil-based binder for organic coating materials.

Table 4
Film properties of the styrenated oils prepared under controlled and conventional styrenation conditions.

Film properties	BO-RAFT2	BO-RAFT0
Drying time[a] (set to touch)	4 min 21 s	5 min
Adhesion[b]	5B	4B
Flexibility[c]	1 mm	1 mm
Water resistance[d]	20 min	Whitening does not disappear within 24 h
Acid resistance[e]	32 min	11 min
Alkali resistance[f]	nc	nc
Hardness (Rocker hardness)	24	10

nc: no change (this states that the film did not undergo any deformation or corrosion).
[a] The test was carried out at 25 °C and 60% relative humidity.
[b] Test method B was applied.
[c] The diameter of the cylinder that caused no crack on the film.
[d] Time for disappearance of whiteness.
[e] The test was carried out at 25 °C with 9% H_2SO_4 solution during 24 h.
[f] The test was carried out at 25 °C with 5% NaOH solution during 24 h.

4. Conclusions

In this study, an air-blown linseed oil was styrenated by the RAFT technique in the presence of PMDC. The hydroperoxide groups formed in the oil molecules served as a macroinitiator in the polymerization process. Better control over structure and molecular weight was obtained when an equivalent amount of PMDC to free radicals was used. In addition to, the film properties of the sample prepared in the controlled manner were better than those produced in the uncontrolled manner. As a result, styrenated oil with a controlled structure, relatively narrow polydispersity and enhanced film properties could be obtained using the RAFT polymerization technique.

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