SOLUBLE POLYMERS FROM A MULTIFUNCTIONAL NATURAL OIL

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ABSTRACT

Vernonia oil, an epoxy functional natural oil, was reacted with substituted monocarboxylic acids with the objective of producing low molecular weight multifunctional esters. Instead, low molecular weight soluble polymers were obtained in good to excellent yields. Reaction occurs through the epoxy groups as shown by spectroscopy and titration. Polymer was produced when the mole ratio of carboxylic acid groups to epoxy groups was 1/3, 2/3, or 3/3.

Key Words: Vernonia oil; Carboxylic acid; Polymerization.

INTRODUCTION

Vernonia oil is a naturally occurring material extracted from the seeds of the vernonia galamensis plant. Vernonia galamensis grows well in the arid and semi-arid regions of the tropics and is indigenous to Africa, Asia, and India [1, 2]. Vernonia oil is one of only two known naturally occurring epoxidized seed oils and has the structure shown in Figure 1.

The combination of epoxy groups and double bonds in the vernonia oil molecule makes it a unique starting material for a variety of potentially useful synthetic transformations. We chose to investigate the reaction of substituted monocarboxylic acids with the epoxy groups of vernonia oil as a way of synthesizing multifunctional esters. We expected to obtain the material(s) shown in Scheme 1 [3, 4].
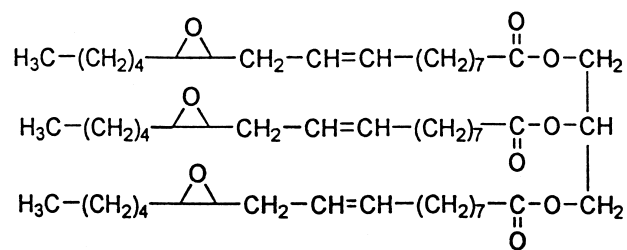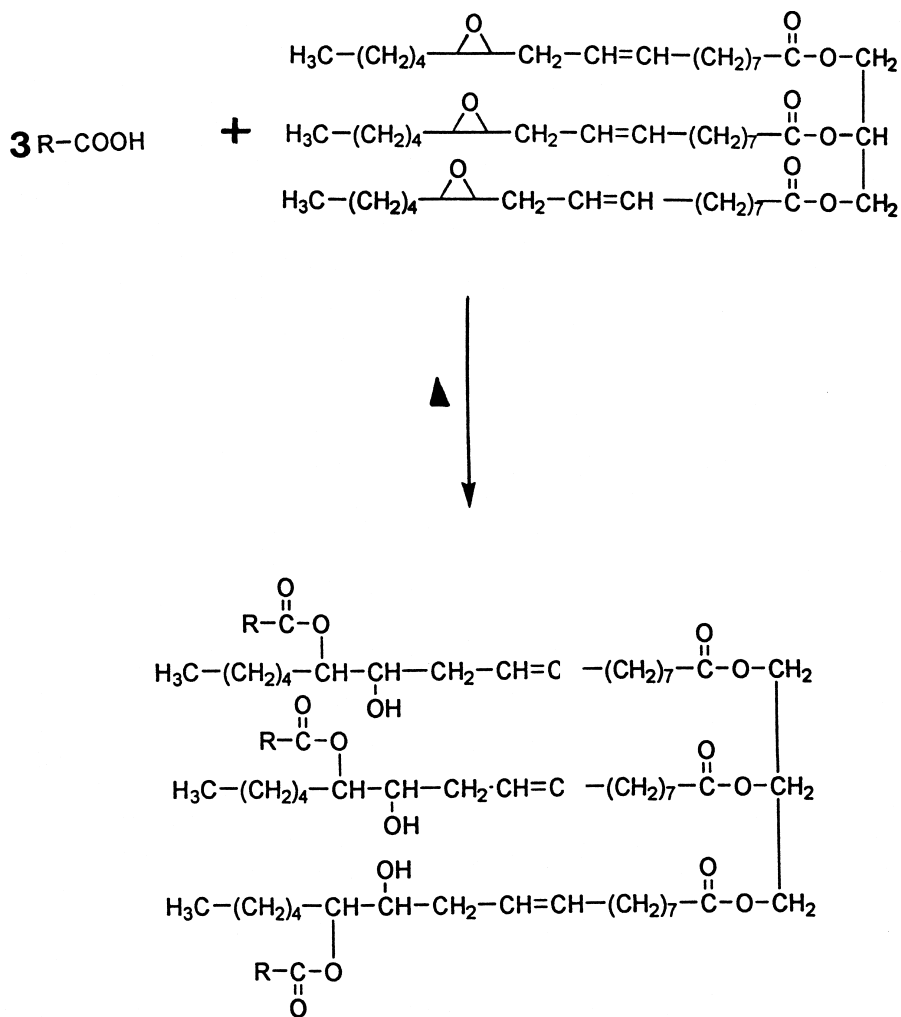
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*Corresponding author.

Figure 1. Structure of vernonia oil.

Scheme 1. Expected synthetic products.

However, when we attempted this reaction, we obtained low molecular weight soluble polymers. The polymeric products were obtained in good yields, in fact, in many cases, polymer was the principle reaction product. As this result was unexpected, we decided to investigate the reaction further. This paper reports our results to date.

EXPERIMENTAL

General

All chemicals besides the vernonia oil were obtained from Aldrich and were used as received. The vernonia oil was obtained from Ver-Tech of Piano, Texas as a 98% pure material and was used as received. The NMR spectra were obtained at ambient temperature on $CDCl_3$ (5–10% w/v) solutions with a Varian Gemini 300 FTNMR. Molecular weights were measured by GPC. The GPC was equipped with a Waters 510 pump and 410 RI detector and two 30cm Polymer Labs Linear columns. Numerical values for the molecular weights were obtained by comparison to a polystyrene calibration curve. Glass transition temperatures were measured with a TA Instruments 2990 DSC.

Polymer Synthesis

A typical polymer synthesis was performed as follows: vernonia oil (100 g) was charged to a 500 ml flask equipped with a mechanical stirrer, reflux condenser and thermometer. Sufficient monocarboxylic acid to react with 1–3 of the epoxy groups was then added followed by 1–1.2 g of tetrabutylammonium halide salt. The contents of the flask were heated to 130ºC. When this temperature was reached, an exotherm occurred that caused the temperature of the reaction mixture to suddenly increase 30–40º. External heating was immediately discontinued and the exotherm subsided after ~10 minutes. External heating was then resumed. The reaction mixture was maintained at 130ºC for 3–3.5 hours. The flask contents were then cooled to ambient temperature, at which point the reaction mixture was a very viscous semi-solid. Polymer was isolated by dissolving the reaction mixture in $CHCl_3$ (200 ml) and adding this solution to excess CH_3OH The polymer was purified by two reprecipitations from $CHCl_3$ solution into CH_3OH. The purified polymer was dried *in vacuo* at 35ºC for 96 hours, then weighed to determine conversion.

RESULTS AND DISCUSSION

The carboxylic acids used in this study are shown in Figure 2. The yields of polymer obtained, molecular weights and glass transition temperatures are summarized in Table 1.

Table 1. Polymer Data

Polymer	Acid	Catalyst[c]	Conversion (wt %)[d]	M_n	M_w	M_w/M_n	Tg (°C)
1	DNBA	TBAB	65	3800	5900	1.55	−23
2	DNBA	TBAI	67	5500	7800	1.42	−16
3	DNBA	TBAC	60	5100	7200	1.41	−21
4	DNBA	—	73	6700	11500	1.72	—
5	CAA	TBAB	64	5700	8100	1.42	—
6	CAA[a]	TBAB	43	1300	1800	1.38	−29
7	HBA[b]	TBAB	45	7900	18600	2.35	−31
8	BA	TBAB	23	4100	4500	1.10	−29

[a] This reaction was conducted in 1,2-dichlorobenzene solution (50% solution).

[b] This reaction was conducted at 180°C in order to obtain a homogeneous reaction mixture.

[c] TBAB = Tetrabutylammonium bromide; TBAI = Tetrabutylammonium iodide; TBAC = Tetrabutylammonium chloride.

[d] Conversion of starting material mass to polymeric products.

Non-polymeric products were also obtained in these reactions. Table 2 lists the yields and molecular weights of these products. The yields and molecular weights of these materials were determined by GPC of crude reaction mixtures. The non-polymeric molecular weight expected for three moles of acid, DNBA e.g., reacted with all the epoxy groups in 1 mol of vernonia oil is ~1560. The molecular weights obtained, considering they are estimated by comparison to a polystyrene calibration curve; approximate the calculated molecular weights of the non-polymeric acid-vernonia oil adducts we expected to obtain as principle reaction products.

We thought that the yield of polymeric products could be related to the PK_a of the organic acid used. Table 3 lists the PK_a's of these acids [5].
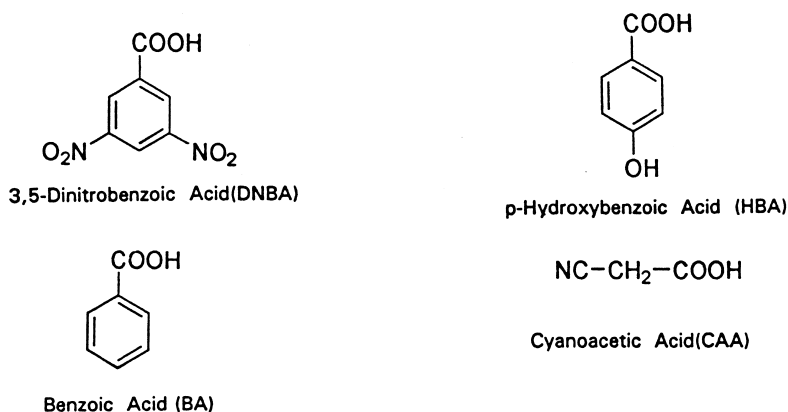

Figure 2. Acid structures.

Table 2. Yields and Molecular Weights of Non-Polymeric Products

Acid	Catalyst	Yield (wt %)	M_n	M_w
CAA	TBAB	30.0	1600	1800
DNBA	TBAI	13.4	1600	1700
HBA	TBAB	16.5	1700	1900
BA	TBAB	69.0	1500	1700
DNBA	—	16.9	1500	1600

It does seem that the polymer yield is influenced by the PK_a of the acid employed. The stronger acids, DNBA and CAA, produce the highest yields of polymer. However, HBA yields the polymer with the highest molecular weight. This might be related to the temperature the HBA reaction was conducted at, but a reaction with BA at 180ºC did not produce a polymer with a molecular weight significantly different than that of the polymer produced with this acid at a lower temperature. It should be noted that the values reported in Table 1 are the average of at least two experiments. The molecular weights obtained from the two HBA polymerizations were ~ ± 15% of the average value reported in Table 1. This still makes these polymers the highest molecular weight species produced in this study. Exactly why this is so is not understood at this time.

In order to ascertain what kind of polymer was being produced, i. e., was polymerization occurring through the double bond or through the epoxy groups, we titrated the epoxy groups before and after the reaction and recorded the ^{1}H-NMR spectra of the polymers.

Titration of the epoxy groups of vernonia oil prior to reaction with acid yields a value of 0.24 epoxy groups/100 g of sample. The epoxy values after reaction with some of the acids are given in Table 4. The ratio of acid functionality to epoxy functionality was 1/1 (mol ratio) for each of the reactions listed in the Table. The values given account for the weight of the added acid.

These results strongly suggest that the polymerization proceeds through the epoxy groups of the vernonia oil. Confirmation that this is so was obtained by ^{1}H-NMR spectroscopy, Figure 3. The resonance due to the double bond protons (d = 5.15–5.85) has not changed in appearance or intensity from that of unreacted

Table 3. Acid PKa's and Polymer Yields

Acid	PKa	Polymer Yield
DNBA	2.85	66.0[a]
CAA	2.46	64.0
HBA	4.58	45.0
BA	4.23	23.0

[a] Average yield of four polymerizations

Table 4.   Epoxy Filtration Results

Acid	Epoxy Value (g/100g of sample)
DNBA	0.003
CAA	0.010
HBA	0.015

vernonia oil. However, the proton resonance assigned to the oxirane group (d = 2.80) [6, 7] is significantly reduced in intensity or has disappeared completely.

Having established that polymerization occurs through the epoxy groups of vernonia oil, it is reasonable to assume that gel should be obtained in some of these reactions; at least in the cases of higher conversion. According to Flory (8), conversions exceeding 50% for trifunctional materials should produce gelation. The titration and NMR data clearly show that the conversion of the epoxy groups exceeds 50% in all cases. Some of the reactions involving the epoxy groups are not polymerization reactions so gel can be avoided in cases of high epoxy group consumption but relatively low polymer yield. In other cases, the vernonia oil must not behave as a trifunctional species i.e., some of the epoxy groups must be consumed before polymerization occurs. Is a reaction with acid necessary prior to polymerization? In experiments without added acid no polymer is produced. Even adding the tetrabutylammonium salt catalyst produced no polymer when the acid was not present. So, an acid-epoxy reaction seems to be required before polymerization can occur. Is it then necessary to add 3 mols of carboxylic acid to one mole of vernonia oil to produce polymer? We reacted 1, 2 or 3 mols of DNBA with 1 mol of vernonia oil to ascertain the effect of stoichmetry on polymer yield. The results obtained are summarized in Table 5.

The results show that 1, 2, or 3 moles of acid produce high yields of polymer with similar molecular weights. It also shows that 3 mols of acid are not necessary. In fact, if all 3 mols of acid reacted with one mole of oil, no polymer would ever be produced. Proton NMR spectra of the polymers produced are shown in Figure 4. The spectrum for the polymer produced from 1 mole of DNBA/mole of vernonia oil shows that only one acid moiety is attached to the polymer per oil molecule. The spectrum of the 2/3 acid/epoxy group mole ratio product is shown in Figure 4B. This spectrum shows that two acid moieties per oil molecule are attached to the polymer. The 3/3 mole ratio polymer spectrum is shown in Figure 3B. This spectrum shows that only two acid moieties per oil molecule are attached to the polymer chain. This result is expected as in order to produce polymer at least one epoxy group per vernonia oil molecule must be available to propagate polymerization. It seems then that the initiation site for polymerization is the acid-epoxy group adduct on the fatty acid chain. This adduct must form somewhat more rapidly than polymerization occurs, otherwise excess epoxy groups would
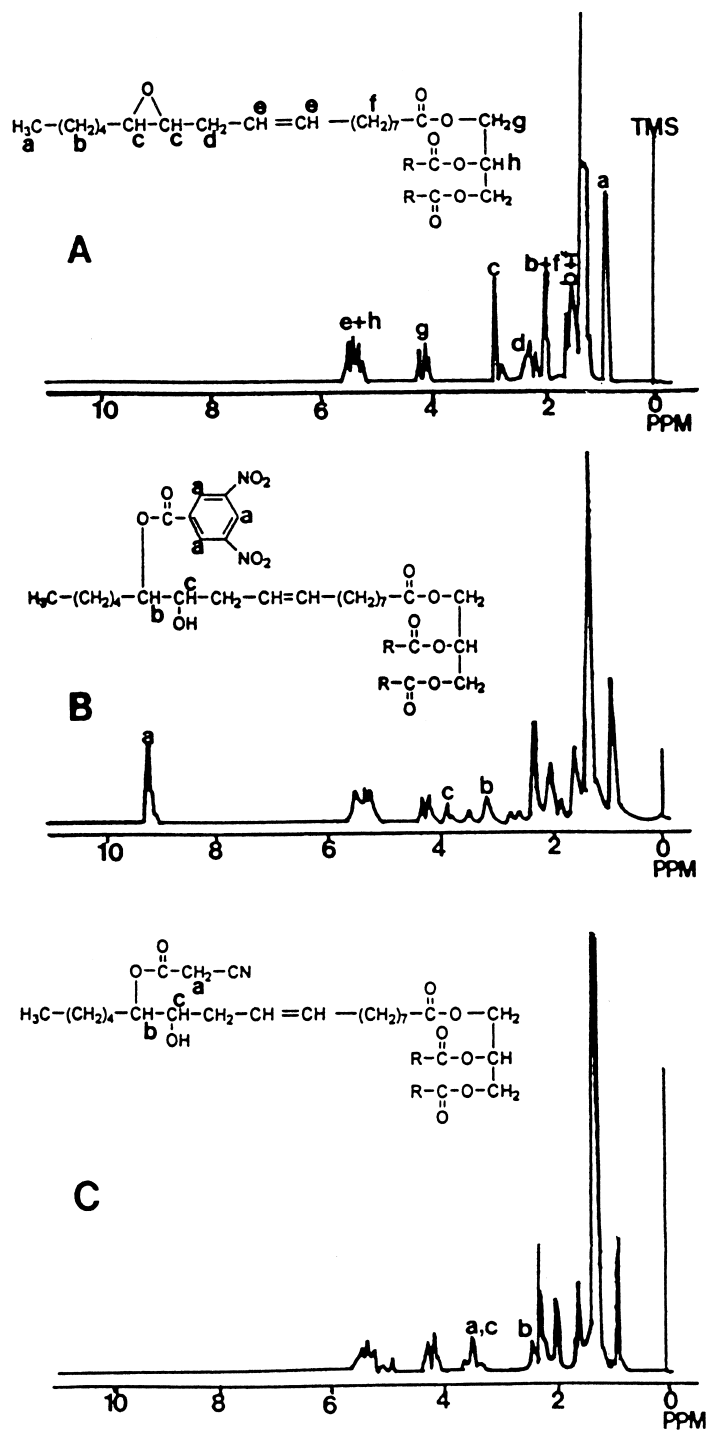
Figure 3. 300 MHz ^{1}H-NMR of: A) vernonia oil; B) vernonia oil and DNBA polymer; C) vernonia oil and CAA.

Table 5. Stoichometry Experiments

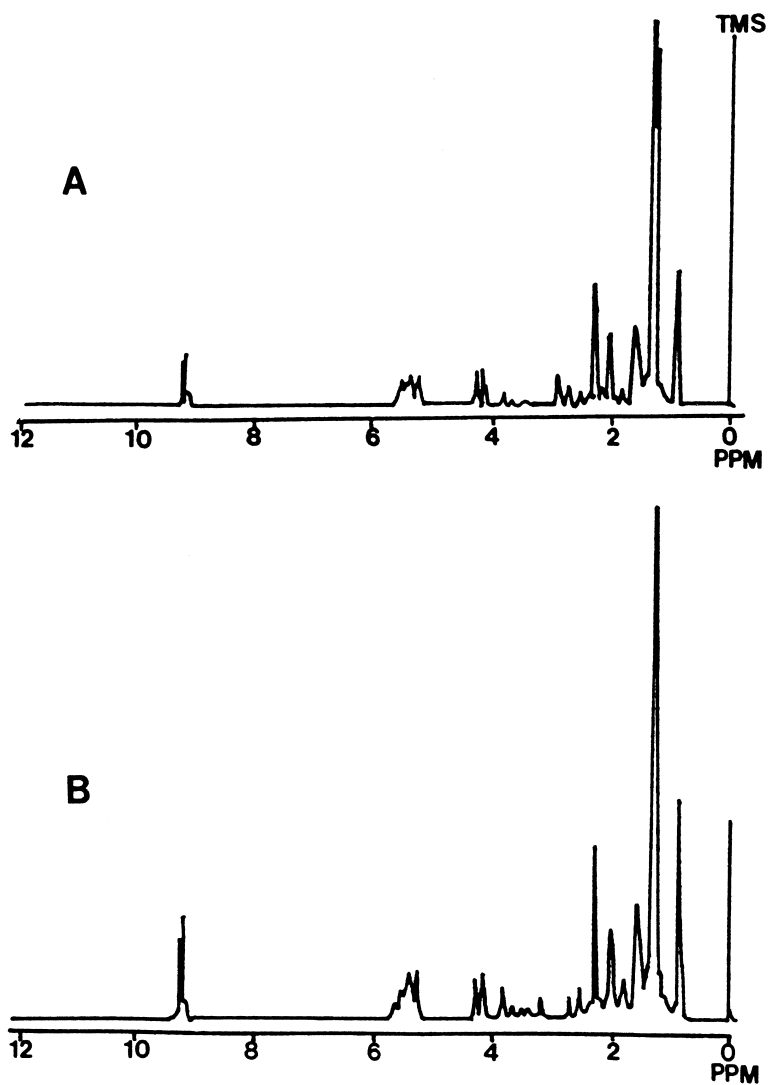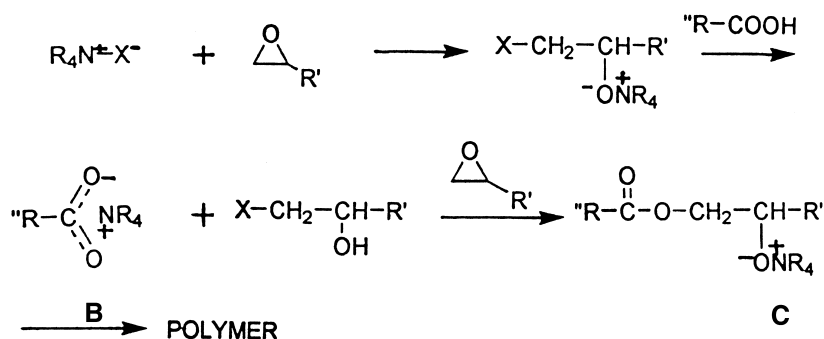| Acid/Epoxy Ratio (mole)	% Yield of Polymer	M_n	M_w
0.33	58.6	4300	5300
0.67	70.0	4900	6200
1.00	69.0	5000	6700

Figure 4. 300 MHz ^{1}H-NMR of: A) vernonia oil and DNBA, 1/3 mole ratio; B) vernonia oil and DNBA, 2/3 mole ratio.

Scheme 2. Proposed reaction mechanism.

cause gelation. However, once the concentration of the acid moiety falls to a certain level, polymerization becomes competitive in a rate sense. This would account for polymerization occurring at a 1/1 mole ratio of acid groups per epoxy groups. An obvious question would be why does the 1/3 ratio (acid/epoxy group) not produce gel as there are two unreacted epoxy groups/oil molecule left? Examination of spectrum 4A shows that there are some unreacted epoxy groups still present in the polymer (d = 2.90). Integration shows this resonance is due to ~1.0 epoxy group. Why this group remains unreacted is not known at present. The epoxy groups of vernonia oil are sterically hindered and not as reactive as, say, bisphenol based epoxies [1, 2] perhaps with more severe reaction conditions this remaining group would react and yield gel.

Nakagawa *et al.* [9], have proposed a possible mechanism for this reaction which is shown in Scheme 2.

In the present case, the reaction mechanism seems to be somewhat different. The tetrabutylammonium catalyst is present in much smaller amounts than the acid is, so all the acid would not be converted to salt B at the same time. But as the ^{1}H-NMR evidence indicates, most of the charged acid becomes part of the polymer (the spectra were recorded on highly purified polymer so the aromatic resonance's are due to bound acid). It would seem that adduct C could react with acid to produce salts like B. In effect, this would be a termination reaction relative to polymerization. The polymerization conducted without added tetrabutylammonium catalyst supports such an idea. The highest yield of polymer and highest molecular weight were obtained from this polymerization. This result also means that some of the acids used are capable of initiating polymerization themselves without added catalyst. This could be the reason that the acids with the higher PK_a's give greater yields of polymer i.e., termination is less effective. Therefore, it seems that the reaction mechanism proposed above is probably operating but is not solely responsible for the results obtained. [Note: It is possible that the ammonium salt concentration is controlling this reaction. If a 1/1 ratio of ammonium salt to acid was used, the desired esters might be produced as all the acid would or could be converted to B.]

CONCLUSION

Attempts to synthesize derivatives of vernonia oil through reaction of functional monocarboxylic acids led to the formation of low molecular weight soluble polymers. The polymers were produced in moderate to good yields. The amount of polymer obtained seems to be related to the PK_a of the acid used. The higher PK_a acids produced greater yields of polymer. Epoxy group titration and ^{1}H-NMR spectroscopy showed that reaction occurs through the epoxy groups of the oil and that the acid becomes part of the polymer. The reaction mechanism proposed by Nakagawa and coworkers partially, but not totally, explains the results obtained.

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