

Allyl Esters of Crambe-Derived Long-Chain Fatty Acids and Their Polymers

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Synopsis

Allyl esters of erucic, brassidic, behenic, oleo-erucic, and stearo-behenic acids, prepared by refluxing benzene solutions of the acids with excess allyl alcohol in the presence of *p*-toluenesulfonic acid monohydrate, polymerize smoothly in the presence of 5 wt. % *t*-butyl perbenzoate at 120°C for 24 hr. Polymerization of the unsaturated acid esters involves a large portion (ca. 84%) of allylic and a small portion (ca. 26%) of ethylenic bonds. The products, saturated and unsaturated, have a degree of polymerization between 6 and 10 and are soluble in typical polymer solvents. Crystallinity, judged by thermal analysis, decreased with increased cis unsaturation. The oligomers melted between -30°C and 59°C and started decomposing at 200°C.

INTRODUCTION

Modern interest in allyl esters of monocarboxylic acids ($\text{RCOOCH}_2\text{CH}=\text{CH}_2$) can be traced to 1945 when allyl alcohol became available in bulk quantities. Past studies focused on unsaturated¹ and saturated² acid esters and gave particular attention to allyl acetate.³⁻⁸ Allylic esters generally polymerize to give products with low molecular weight because of degradative chain transfer.⁴ Polymerization may be especially difficult under certain conditions, as Chow and Marvel reported after studying allyl undecanoate.⁹

Monomeric and oligomeric allyl esters both possess properties suitable for specialized applications: allyl caproate, synthetic fruit (pineapple) flavor¹⁰; allyl palmitate and allyl stearate, extreme-pressure lubricity¹¹; poly(allylcaprylate), low pour point lubricity.¹²

Availability of crambe-derived acids¹³ prompted us to prepare new allyl esters. These products will utilize fatty acids obtained from a potential new crop and yield novel prepolymers or polymers with potential industrial uses. Here we wish to report their preparations as well as fine structure and thermal properties determined by nuclear magnetic resonance (NMR) and differential scanning calorimetry/thermogravimetric analysis, respectively.

EXPERIMENTAL

Materials

Erucic acid, technical grade (Banta, Denmark; 81 ± 3% pure), was purified by low-temperature crystallizations from acetone:water (5:1).¹⁴ The collected precipitate, assayed by gas-liquid chromatography (GLC) of the methyl ester, was 94.7% pure.

Brassicic acid was prepared by a *cis*-*trans* isomerization of the purified erucic acid.¹⁵ Infrared (IR) quantitation of the isomerized product indicated *trans* content of 96.3%.

Behenic acid was prepared by hydrogenation of purified erucic acid (150 g) with 1 wt. % Rufert nickel as catalyst at 150°C under 2000 psi for 6 hr. The hydrogenation product was crystallized from boiling toluene (10 ml/g) to give behenic acid in 93.31% yield and 97.8% purity. The elemental analysis and IR spectrum¹⁶ were deemed satisfactory.

Oleo-erucic acid prepared here by saponification of crambe oil contained 14% oleic acid, 69% erucic acid, and 17% other acids; iodine value, 91.6; neutralization equivalent, 306.

Stearo-behenic acid was a crude commercial mixture containing 25% stearic, 59% behenic, and 16% homologous acids according to our GLC analysis. This mixture simulated that obtainable by hydrogenation of the oleo-erucic acid; neutralization equivalent, 322.

Allyl Esters

Preparation

Into a 2-liter, single-necked flask equipped with a Barrett moisture trap and a condenser were introduced 1 mole or 1 neutralization equivalent of the acid and 2 moles (135 ml) allyl alcohol, along with 0.03 mole (5.7 g) *p*-toluenesulfonic acid monohydrate as catalyst and 750 ml benzene as entraining agent. While stirring with a magnetic bar, the mixture was refluxed for 8 hr, after which no more water was collected.

The reaction mixture was washed with water to remove the excess allyl alcohol and catalyst; the solid product from behenic or stearo-behenic acid was dissolved in 300 ml ethyl ether before washing. The crude ester was then distilled under vacuum in the presence of 0.5 wt. % Ionox 330 (Shell Chemical Co.; mp 244°C. During the distillation of allyl behenate or stearo-behenate, hot water was used as condenser coolant. The center cut was obtained in a yield of 85%–90%.

Characterization

Composition of the distilled esters was determined by GLC with a Hewlett-Packard Model 5750 chromatograph equipped with a flame ionization detector. The nonpolar column ($\frac{1}{8}$ in. \times 10 ft, stainless steel) was packed with 5% Apiezon L on acid-washed, silylated 60/80-mesh Chromosorb W and was maintained at 240°C. The polar column ($\frac{1}{4}$ in. \times 12 ft, stainless steel) was packed with 5% LAC-2-R 446 on acid-washed, silylated 60/80-mesh Chromosorb W and was maintained at 185°C. Methyl *n*-alkanoates were used as references for the identification of components.¹⁷

IR spectra were recorded with a Perkin-Elmer Model 137 spectrophotometer from thin films or KBr pellets. NMR spectra were secured on carbon tetrachloride solutions with a Varian HA-100 spectrometer. Ultraviolet (UV) spectra were obtained with a Beckman DK-2A spectrophotometer from cyclohexane solutions in 0.2-cm sample path length quartz cells under nitrogen at a flow rate of 50 ft³/hr.

Saponification equivalents,¹⁸ iodine values,¹⁹ and physicochemical properties were determined by the conventional methods.

Homopolymers

Preliminary polymerizations designed to find an efficacious initiator and the proper reaction temperature were carried out as follows: A mixture of monomer, 3 g, and initiator, 2.5, 5, or 10 wt. %, was introduced into a test tube. Under a blanket of nitrogen, the mixture was heated to 80 or 120°C. The reaction was followed by changes in the refractive index (n_D^{40}). When the refractive index ceased to increase, the reaction was terminated.

Polymerization

Into a 1-liter, three-necked flask equipped with a nitrogen inlet and a thermometer were introduced 380 g of the monomer and 20 g (5% total wt.) *t*-butyl perbenzoate (BPB). While being stirred with a magnetic bar, the mixture was heated at 120°C for 24 hr.

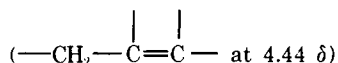
The liquid reaction products from unsaturated acids, namely, allyl erucate, allyl brassidate, and allyl oleo-erucate, were washed with 3 liters 95% ethanol in three portions, followed by solution into 250 ml tetrahydrofuran and precipitation with 3 liters 95% ethanol. The solid reaction products, i.e., allyl behenate and allyl stearo-behenate, were swelled in 3 liters tetrahydrofuran and washed with a total of 18 liters 95% ethanol. After removal of solvent, 235 g (62% of theory) poly(allyl erucate), 261 g (69%) poly(allyl brassidate), 82 g (22%) poly(allyl oleo-erucate), 185 g (97%) poly(allyl stearo-behenate) were obtained.

Characterization

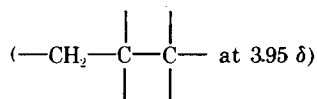
The number-average molecular weight was determined in benzene solution at 37°C with a Mechrolab Model 301A vapor pressure osmometer. The viscosity was measured with a LVF Brookfield Synchro-Lectric viscometer at 25°C. The solubility of 0.1 g polymer in 2 ml solvent was secured with the aid of a Vortex Genie Mixer.

Infrared quantitation of trans bonds was as follows: 50 mg polymer was dissolved in 1-ml carbon disulfide. The solution was filled into a 0.2-mm NaCl cell. After the ester-C—O—C absorbance at 8.56 μm was adjusted to 0.500, the trans absorbance at 10.36 μm was recorded at slow speed. The unchanged trans double bond was then calculated by comparison with the trans absorbance of the monomeric allyl brassidate recorded similarly.

Free allylic methylene protons



and the bonded allylic methylene protons



were measured by integrating the appropriate NMR signals.

The calorimetric analysis was carried out with a Perkin-Elmer differential

scanning calorimeter Model 1B after calibration with indium (156°C, $\Delta H = 6.79$ cal/g)²⁰ and lead (327°C) as standard. The sample, about 15 mg, was weighed into an aluminum pan; an empty pan served as reference. DSC curves were obtained with the range set at 8, nitrogen flow rate at 30 ml/min, and chart speed at 8 in./hr. Samples were cooled with liquid nitrogen.

Thermogravimetric analyses were performed on a Cahn RG electrobalance that was calibrated with Alumel (163°C), nickel (354°C), and MuMetal (393°C) standards. The sample size was 1.8 ± 0.2 mg; recorder range, 2; nitrogen flow rate, 50 ml/min; chart speed, 4 in./hr.

For programmed thermogravimetry, and scan speed was 5°C/min from 20 to 500°C after which the temperature was held constant. Isothermally, the scan was started after the sample was heated (80°C/min) to the desired temperature; i.e., 200, 300, and 400°C.

The allyl esters and the derived liquid polymers were incorporated into commercial poly(vinyl chloride) resin (Geon 101) at 32% level²¹ and were compared with resin samples containing three known plasticizers, i.e., dioctyl phthalate, Santicizer 405 (polyester), and bis(2-methylpentyl) brassylate.

RESULTS AND DISCUSSION

Five allyl esters, which were prepared by esterification and purified by vacuum distillation, showed no inhibitor contamination when analyzed by IR. The purified esters, light yellow in color, retained their olefinic configuration. Table I lists the GLC and chemical analyses, which agree well with calculated values. Table II gives the physical properties.

Identification of Allylic and Olefinic Double Bonds

Careful identification and differentiation of allylic and olefinic double bonds were necessary because of the possibility of allyl-propenyl isomerization, as is known to occur in ethers²²⁻²⁴ and during elaidinization of the olefinic bond in unsaturated esters.²⁵ IR spectra (Fig. 1, II, IV, and VI) showed absorptions of allyl esters, terminal C=C stretching at 6.10 μm , and terminal CH=CH₂ out-of-plane deformations at 10.13 and 10.78 μm which are clearly different from those due to trans bonds, at 10.36 μm or cis bonds, at 3.03 μm ,²⁶ 5.98 μm ,²⁴ or 6.05 μm ,²⁷ as reported for ester propenyl.

The UV absorptions, $\lambda_{\text{max}}^{\text{cyclohexane}}$ (ϵ_{max}), of allyl erucate, brassidate, behenate, oleo-erucate, and stearo-behenate were 189 nm (11,000), 189 nm (12,000), 182 nm (7700), 190 nm (9800), and 182 nm (7000), respectively. A higher ϵ_{max} for the trans than for the cis isomer is in agreement with the theory that the less hindered the π electron system, the more intense is its absorption.²⁸ These results are in favor of the allyl esters, because a propenyl ester (—COO—CH=CHCH₃) possesses a $n-\pi$ conjugation that will result in a higher ϵ_{max} at a longer λ_{max} .

The NMR spectrum of the allyl erucate (curve I, Fig. 2) is an example for the allyl esters. The chemical shifts are: 5.24 δ (1H, *m*, $J_{AB} = 3.1$ cps, $J_{AX} = 12.0$, H_A), 5.10 (1H, *m*, $J_{BX} = 17.0$, H_B), 5.84 (1H, *m*, H_X), 4.44 (2H, *d* of *t*, $J_{AC} = 1.6$, H_C), 2.23 (2H, *t*, $J_{\alpha\beta} = 7.0$, H _{α}), 1.58 (2H, *t*, $J_{\beta D} = 7.0$, H _{β}), 1.25 (28H, *s*, H_D), 1.97 (4H, *d*, H_E), 5.26 (2H, *m*, H_F), and 0.86 (3H, *t*, H_G). They are similar to

TABLE I
Gas-Liquid Chromatographic and Chemical Analyses of Allyl Esters

| Ester | Major components, % ^a | | Mol. wt. | Sap. eq. | Iodine value | | C, % | | H, % | |
|-----------------------|---|---|----------|----------|--------------------|--------------------|-------|-------|-------|-------|
| | A | B | | | Calcd ^b | Found ^c | Calcd | Found | Calcd | Found |
| Allyl erucate | 95.3% C _{22:1} ^{13c} | 97.5% C _{22:1} ^{13c} | 378.64 | 355 | 134.1 | 131.2 | 79.30 | 79.50 | 12.25 | 12.38 |
| Allyl brassidate | 94.7% C _{22:1} ^{13c} | 97.5% C _{22:1} ^{13c} | 378.64 | 372 | 134.1 | 130.9 | 79.30 | 79.32 | 12.25 | 12.45 |
| Allyl behenate | 96.6% C _{22:0} | 96.2% C _{22:0} | 380.66 | 374 | 66.7 | 64.0 | 78.88 | 78.73 | 12.71 | 12.66 |
| Allyl oleo-erucate | 70.2% C _{22:1} ^{13c} + 19.3% C _{18:1} ^{9c} + C _{18:2} ^{9c,12c} + C _{18:3} ^{9c,12c,15c} | 71.6% C _{22:1} ^{13c} + 20.4% C _{18:1} ^{9c} + C _{18:2} ^{9c,12c} + C _{18:3} ^{9c,12c,15c} | — | 329 | — | 147.7 | — | 79.17 | — | 12.44 |
| Allyl stearo-behenate | 58.1% C _{22:0} + 25.7% C _{18:0} | 62.1% C _{22:0} + 23.3% C _{18:0} | — | 347 | — | 71.3 | — | 77.98 | — | 12.60 |

^a Determined by gas-liquid chromatograph equipped with (A) a 5% Apiezon L. column at 240°C and (B) a 5% LAC-2-R 446 column at 185°C; calculated as area %.

^b Based on pure compound.

^c Average of two determinations.

TABLE II
Physical Properties of Allyl Esters

| Ester | mp, °C | bp, °C/mm | Density | n_D | | Solubility in 10 parts ^a | | | | | | | |
|-----------------------|-----------|--------------|----------------------|--------|--------|-------------------------------------|---|---|---|---|---|---|---|
| | | | | 40°C | 60°C | a | b | c | d | e | f | g | |
| Allyl erucate | 10.8-11.2 | 186-196/0.2 | 0.8685 ²⁰ | 1.4522 | 1.4445 | P | P | S | S | S | S | S | S |
| Allyl brassidate | 26.8-27.2 | 192-194/0.3 | 0.8667 ⁴ | 1.4514 | 1.4438 | I | P | S | S | S | S | S | S |
| Allyl behenate | 48.3-49.1 | 202/0.4 | — | — | 1.4384 | I | P | P | P | S | S | S | S |
| Allyl oleo-erucate | 8.4-8.7 | 170-197/0.1 | 0.8703 ²⁰ | 1.4530 | 1.4456 | P | P | S | S | S | S | S | S |
| Allyl stearo-behenate | 39-45 | 155-204/0.2 | — | — | 1.4374 | I | P | P | S | S | S | S | S |

^a a = Water; b = methanol; c = ethanol; d = acetone; e = benzene; f = ethyl ether; g = tetrahydrofuran; I = insoluble; S = soluble; P = partially soluble.

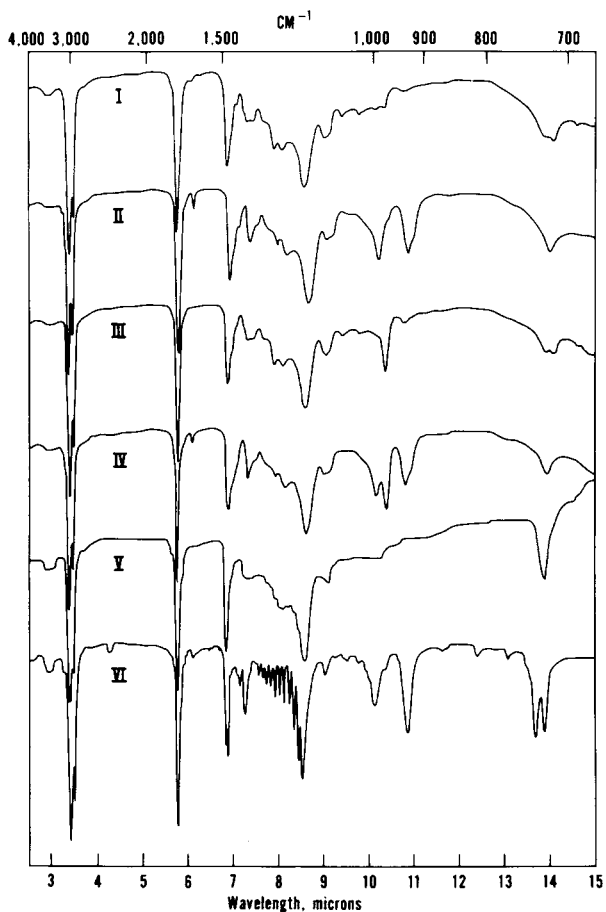


Fig. 1. Infrared spectra: (I) poly(allyl erucate) (film); (II) allyl erucate (film); (III) poly(allyl brassidate) (film); (IV) allyl brassidate (film); (V) poly(allyl behenate) (KBr pellet); (VI) allyl behenate (KBr pellet).

the reported chemical shifts for oleic acid²⁹ and diallyl ether,³⁰ except that absorption of H_C shifts to the lower field ($\Delta\delta$ for $-\text{COOCH}_2-$ = 4.44–3.97 = 0.47; reported $\Delta\delta$ for $-\text{OCH}_2-$ = 0.5).³¹ The splitting pattern and the chemical shift of the H_C unequivocally supports the allyl structure; a propenyl ester would give a lower-field doublet of quartets for the corresponding “single” proton. It would also give a doublet of the doublet near 1.6 ppm³² for the terminal methyl protons adjacent to the carbon-carbon double bond.

Polymerization Characteristics

Great difficulty has been experienced in the polymerization of (a) allyl undecanoate with 1% potassium persulfate or 1% diethyl azobisisobutyrate at 60°C,⁹ (b) allyl esters of saturated fatty acids with 0.5% benzoyl peroxide (PBO) at 50, 65–70, and 85°C,³² and (c) allyl esters of unsaturated fatty acids with 2% BPO at 80°C.¹ We examined three different peroxides, i.e., BPB, dicumyl peroxide (DCPO), and di-*t*-butyl peroxide (DBPO) at 120°C. This reaction temperature

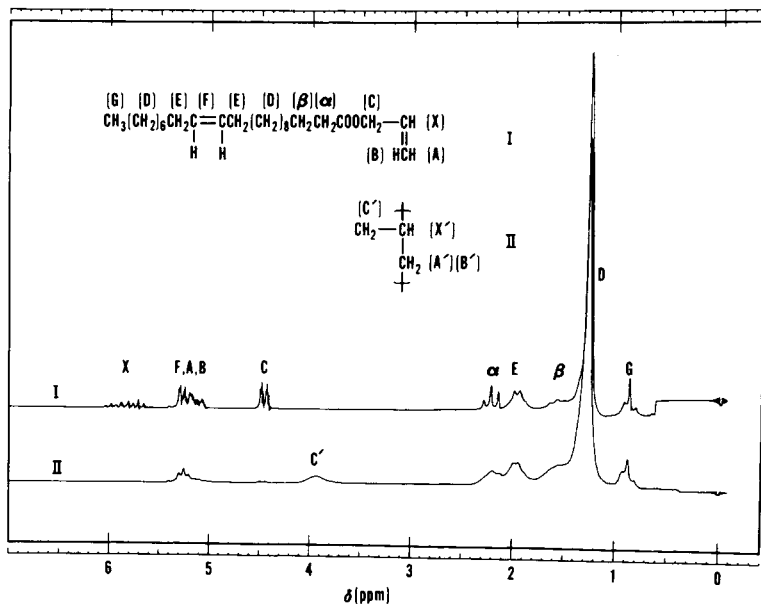


Fig. 2. Nuclear magnetic resonance spectra: (I) allyl erucate; (II) poly(allyl erucate).

was selected on the basis of the initiators' half-lives from which the reaction time was estimated to be five times the half-life. The half-lives for BPB, DCPO, and DBPO at 120°C are 1.6, 5.6, and 20 hr, respectively.

The effectiveness of these initiators compared to BPO and azobisisobutyronitrile (AIBN) was evaluated in terms of an overall change in refractive index (n_D^{40}) during the reaction. Changes for allyl erucate under various conditions are shown in Figure 3. The highest refractive index was obtained with 5% BPB at 120°C. The polymer from the 5% BPB initiated system had the lowest allyl

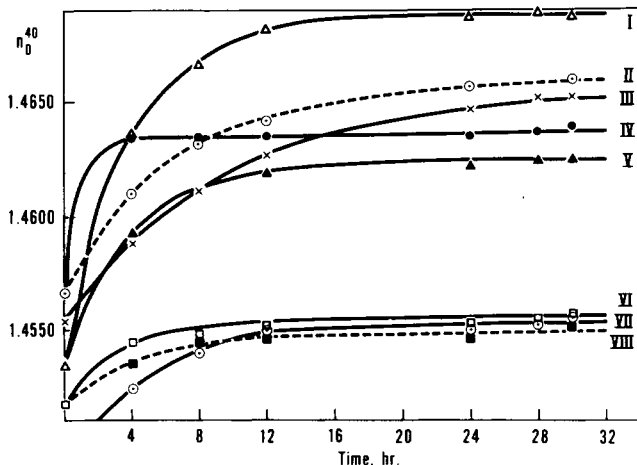


Fig. 3. Refractive indices of products from polymerization of allyl erucate initiated by: (I) 5% *t*-butyl perbenzoate at 120°C; (II) 5% benzoyl peroxide at 80°C; (III) 5% dicumyl peroxide at 120°C; (IV) 5% benzoyl peroxide at 120°C; (V) 2.5% *t*-butyl perbenzoate at 120°C; (VI) 5% azoisobutyronitrile at 120°C; (VII) 5% *t*-butyl peroxide at 120°C; (VIII) 5% azoisobutyronitrile at 80°C.

content and residual unsaturation in comparison to the polymers made with other initiators. These results were corroborated for the polymerization of allyl brassidate as shown in Figure 4.

Five poly(allyl esters) were then prepared by bulk polymerization from 380 g monomer under the established conditions. It should be cautioned that the reaction mixture temperature might surpass the bath temperature by as much as 9°C during the first 2 hr of polymerization. The physicochemical properties of these polymers are listed in Table III.

Fine Structure of Polymers

Whereas the IR spectra of the monomers showed an absorption at 13.95 μm due to the CH_2 rock of the fatty acid chain, the spectra of the polymers showed an additional absorption at 14.10 μm due to the CH_2 rock of the newly formed polymer chain.³³ The polymers also absorbed IR at about 17.2 μm which may indicate an atactic structure of the allylic unsaturation similar to polypropylene³⁴ (17.39 μm), in which the methyl side chain is replaced by the side chain shown in structure II in Figure 2. The polymerized trans bond in poly(allyl brassidate) by IR quantitation was 26%.

The NMR spectrum of poly(allyl erucate), as shown in curve II of Figure 2, demonstrated the slow motion of the rigidly restricted side chains by the loss of fine structure to give broad lines of H_β , H_α , and $\text{H}_{c'}$. The up-field shift of the allylic hydrogens from 4.44 (H_c) to 3.95 ppm ($\text{H}_{c'}$) was obvious evidence for the disappearance of the adjacent double bond that amounted to 84%. The $\text{H}_{A'}$, $\text{H}_{B'}$, and $\text{H}_{X'}$ also shifted up to 1.1–1.8 ppm, based on the published spectrum of *n*-butyl acetate³⁵ but were apparently overshadowed by the H_D , H_β , and H_E in the same area.

The unchanged olefinic (74%) and allylic (16%) double bonds were consistent with the residual unsaturation of the polymer. The iodine value ratios of polymer over monomer were 0.46 and 0.47, respectively, for poly(allyl erucate) and

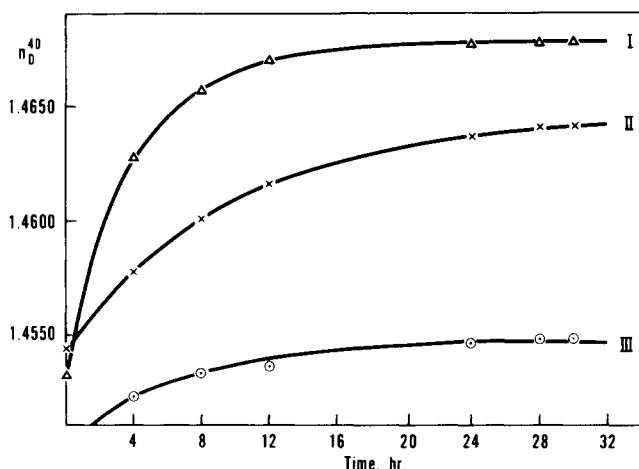


Fig. 4. Refractive indices of products from polymerization of allyl brassidate initiated by: (I) 5% *t*-butyl perbenzoate at 120°C; (II) 5% dicumyl peroxide at 120°C; (III) 5% *t*-butyl peroxide at 120°C.

TABLE III
Physicochemical Properties of Poly(allyl Esters)

| Polymer | Form | n_D^{40} or mp | Viscosity, cps | Iodine value | \bar{M}_n | Solubility in 20 parts ^a | | | | | | | | | | | |
|---------------------------------|--------|------------------|-------------------|-----------------|-------------|-------------------------------------|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | a | b | c | d | e | f | g | h | i | j | k | |
| Poly(allyl erucate) | liquid | 1.4756 | 4790 | 61.8 | 3930 | S | S | S | I | S | S | S | I | I | I | I | S |
| Poly(allyl brassidate) | liquid | 1.4728 | 2375 | 63.0 | 2110 | S | S | S | I | T | S | S | I | I | I | I | S |
| Poly(allyl behenate) | solid | 62-65°C | — | — | — | G | G | G | I | I | I | G | I | I | I | I | I |
| Poly(allyl oleo-erucate) | liquid | 1.4773 | 1330 | 67.8 | 2150 | S | S | S | I | S | S | S | I | I | I | I | S |
| Poly(allyl stearo- behenate) | solid | 56-62°C | — | — | — | G | G | G | I | I | I | G | I | I | I | I | I |

^a a = Benzene; b = carbon tetrachloride; c = chloroform; d = N,N-dimethylformamide; e = 1,4-dioxane; f = ethyl acetate; g = tetrahydrofuran; h = acetone; i = acetonitrile; j = dimethyl sulfoxide; k = carbon disulfide; G = swelling; S = soluble; I = insoluble; T = partially soluble to give a turbid solution.

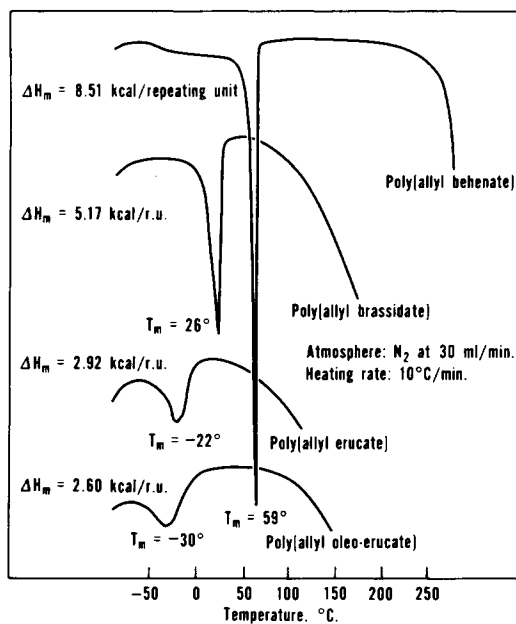


Fig. 5. Thermal characteristics of poly(allyl esters).

poly(allyl brassidate). That these unsaturated polymers were not multiple-crosslinked was deduced from their solubility in benzene, carbon tetrachloride, chloroform, ethyl acetate, and tetrahydrofuran. Thin-layer chromatography (TLC) results indicated broad molecular weight distributions. The degrees of polymerization calculated from the number-average molecular weights for poly(allyl erucate) and poly(allyl brassidate) were 10.4 and 5.6, respectively. These values were lower than the reported degree of polymerization of 13 for poly(allyl acetate).³ This suggests that the rate of abstraction may be faster for the polymerization of allyl esters of unsaturated acids than for the polymerization of allyl esters of saturated acids, because the degree of polymerization is approximately equal to the ratio of the rate of addition to the rate of abstraction.

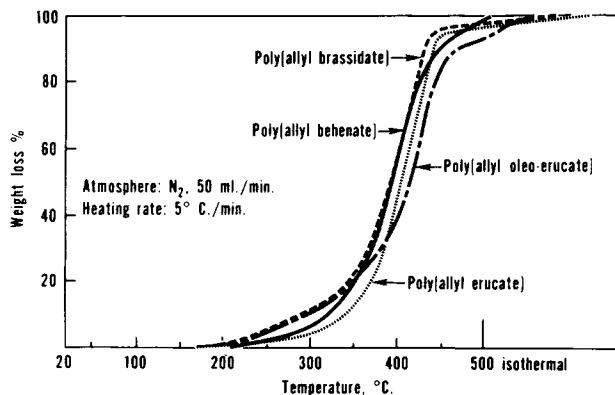


Fig. 6. Thermal stabilities of poly(allyl esters) at programmed temperatures.

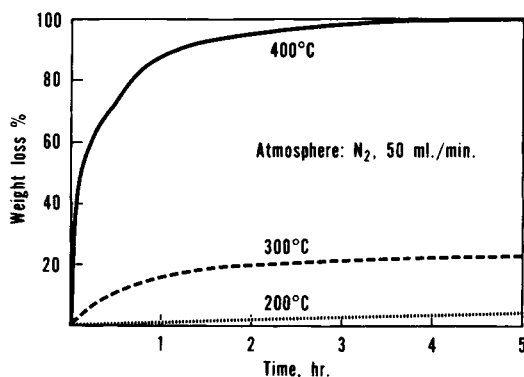


Fig. 7. Thermal stabilities of poly(allyl esters) at isothermal temperatures.

Olefinic (internal) double bonds, which have low polarizability, would not enhance addition significantly, but they might furnish enough additional reactive hydrogens to affect abstraction rates. Subsequent coupling of resonance-stabilized monomeric free radicals to form dimers could further contribute to a low degree of polymerization.

Thermal Properties of Oligomers

Each sample under examination was completely free of solvent. The conditions for differential scanning calorimetry were selected such that an appropriate endothermic peak was produced and the reported ill effect of heating rate^{36,37} was minimized. To compare the heat of melting on the same basis for polymeric materials, we used kcal/repeating unit of oligomer or kcal/mole of monomer, rather than cal/g, even though the latter unit has been used customarily for monomeric materials.

The thermal characteristics are shown in Figure 5. The peak temperatures (T_m) and heats of melting (ΔH_m) were: poly(allyl behenate), 59°C and 8.51 kcal/repeating unit; poly(allyl brassidate), 26°C and 5.17 kcal/repeating unit; poly(allyl erucate), -22°C and 2.92 kcal/repeating unit; poly(allyl oleo-erucate), -30°C and 2.60 kcal/repeating unit. These T_m values were reproduced from immediate repetition with the sample. X-Ray diffraction patterns of these esters revealed their crystallinities. The sharp endotherm of poly(allyl behenate) seems thus to reflect a high degree of crystallinity, whereas the broad endotherms of the cis bond-containing poly(allyl erucate) and poly(allyl oleoerucate) may be due to less efficient molecular packing.

At temperatures above T_m , endothermic drift was more severe with the double bond-containing poly(allyl esters) than it was with poly(allyl behenate), which eventually decomposed rather sharply above 300°C.

The thermal stabilities determined by thermogravimetry at programmed temperature are presented in Figure 6. In each case, weight loss stated at 200°C and became drastic around 400°C. This finding was verified by isothermal (200, 300, and 400°C) thermogravimetry of poly(allyl erucate) as shown in Figure 7. Interestingly, poly(allyl erucate) lost weight slower than did the other polymers up to 400°C even though it was the first to exhibit endothermic drift (specific heat change) after melting (Fig. 6). Aside from such subtle variations that relate

to structural differences, we assume that the thermal degradation of these polymers follows general reaction schemes already published.³⁸

According to tests performed at the Eastern Regional Research Center, allyl erucate, allyl brassidate, allyl behenate, allyl oleo-erucate, allyl stearo-behenate, poly(allyl erucate), poly(allyl brassidate), and poly(allyl oleo-erucate), all being liquid, were noncompatible as external plasticizers for poly(vinyl chloride).

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