

Polymerization of Allyl Esters Derived from Long-Chain Fatty Acids and Palm Olein

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SYNOPSIS

Allyl esters of palm olein, palmitic, and oleic acids were synthesized by transesterification and esterification methods using KOH and absolute H₂SO₄ as catalysts, respectively. Three allyl esters, namely, allyl palmitate, allyl epoxystearate, and epoxidized allyl ester of palm olein, were successfully polymerized in the presence of *t*-butyl perbenzoate at 120°C to obtain oligomers with the average number of backbone atoms approximately equal to the number of skeletal atoms of the long-dangling side chains. The kinetic data of polymerization were conformed to the rate equation proposed by other workers. No oxirane cleavage was detected during the chain reaction. The melting behavior of these comb-shaped polymers was compared with that of their respective allylic monomers. The polymer of epoxidized allyl ester of palm olein exhibits a glass transition temperature at 204.4 K. The critical molecular weights of the polymers of allyl esters investigated are predicted to be not lower than 10⁴.

INTRODUCTION

The free-radical polymerization of allyl compounds including allyl esters is characteristically different from that of the vinyl monomers in that it proceeds with a slower rate and yields relatively low molecular weight products. Kinetically, these are the direct consequences of the formation of an allylic radical by the degradative chain transfer process that would terminate the growing chain radical prematurely.¹

In the early work of allyl polymerization, benzoyl peroxide and *p*-chlorobenzoyl peroxide were widely employed as initiators.²⁻⁸ Recently, Chang and Miwa⁹ established that *t*-butyl perbenzoate (BPB) is indeed more efficient in polymerizing the allyl esters than are the other peroxide and azo compounds. Hence, this particular initiator was applied throughout the following investigations.

A fast transesterification procedure has been developed lately in our laboratory. It allows one to prepare allyl esters such as the allyl esters of palm

olein (ALEPOL) with high yield. Here, we also synthesized the allyl esters of palmitic and oleic acids by an esterification process. Some of these esters were epoxidized, as to eliminate the unsaturation before they were polymerized. In this study, the polymers obtained were characterized by various approaches and their thermal properties were reported.

EXPERIMENTAL

Materials

Reagent-grade solvents were purchased from the reliable sources, and BPB was obtained from Fluka (Switzerland). All these chemicals were used as received without further purification unless otherwise specified. However, reagent grade allyl alcohol supplied by Fluka was distilled from magnesium activated with iodine in a dry N₂ atmosphere. The dry alcohol was stored over molecular sieve 4 A and kept in a dark place before use.

A commercial-grade RBD (refined, bleached, and deodorized) palm olein (POL) was employed. It was dried under reduced pressure to remove the moisture and volatile components before use. It consists

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mainly of triglycerides with the fatty acid content (mol %) documented as follows¹⁰: lauric (0.2), myristic (1.1), palmitic (39.8), palmitoleic (0.2), stearic (4.4), oleic (42.5), linoleic (11.2), linolenic (0.4), and arachidic acid (0.4).

Both oleic and palmitic acids in reagent grade were purchased from Merck (Germany) and used without further purification. Formic acid (99.9%) was obtained from BDH (England). Hydrogen peroxide (30%) was purchased from Fluka, and its concentration was determined by iodometric titration. The absolute H₂SO₄ was prepared by the foggy-fair method.¹¹

Transesterification

ALEPOL was prepared by the following technique: Approximately 7 g of KOH was dissolved in 500 mL allyl alcohol in a round-bottom flask at 60–70°C. Meanwhile, 755 mL palm olein (density at 25°C = 0.901 g/mL) was heated and stirred at the same temperature. The alkoxydized alcohol was then mixed with the oil and the reaction was essentially completed within 1 min. The reaction mixture was transferred into a 2 L separating funnel and washed repeatedly with dilute HCl solution and distilled water until the ester layer was acid-free. The small amount of unreacted alcohol was finally removed by drying under reduced pressure at ambient temperature. The yield was 710 g.

Esterification

Absolute H₂SO₄ was used as the catalyst. The mol ratio of allyl alcohol and fatty acid was 50 : 1, and the absolute H₂SO₄ was 0.5% (w/w) with respect to the fatty acid. The alcohol was mixed with the catalyst before the fatty acid was added. The reaction mixture was refluxed with stirring for 3 h in a N₂ atmosphere. The product was washed with distilled water repeatedly until acid-free. Distillation under reduced pressure was performed with the middle fraction collected at 168 ± 2°C/1 mmHg. This step was repeated twice if necessary. Any side products monitored by a gas chromatography (GC) were efficiently removed by passing the ester through a silver nitrate–silicic acid column. The purity of the final product was confirmed by GC and ¹³C-NMR analysis. The yields of allyl palmitate (ALPMT) and allyl oleate (ALOL) were found to be 76% and 47% with respect to the fatty acids, respectively.

Epoxidation

Epoxy esters were prepared using peroxyformic acid generated *in situ* at ambient temperature (27°C) in the presence of benzene as to minimize oxirane cleavage. The main components were charged accordingly to the proportion in moles of unsaturation: H₂O₂ : HCOOH = 1 : 2.8 : 0.35.¹² Typically, 1 kg of ester was mixed with the required amount of HCOOH and dissolved in 500 mL benzene. While the solution was being stirred at 10–15°C, a designated volume of H₂O₂ (30%) was added dropwise. The mixture was finally warmed to the ambient temperature, at which the reaction was allowed to continue for 30 h. The product was washed repeatedly with distilled water until acid-free. Benzene and water were removed by rotary evaporation and then “under vacuum (~ 1 mm Hg)” at 60°C. This procedure was used to prepare allyl epoxystearate (EPALST) and epoxidized ALEPOL (EPALEPOL), respectively, from ALOL and ALEPOL. On the basis of the fatty acid content cited above for POL, the number-average molecular weight, *M_n*, of EPALEPOL is estimated to be 321.

Polymerization

Polymerization was carried out in a 1 L three-necked round-bottom flask equipped with a N₂ inlet, a condenser, and a thermometer. The vessel was immersed in a silicone oil bath controlled at 120 ± 1°C. An amount of 400 g allyl ester was introduced into the flask and was stirred under N₂ atmosphere for 0.5 h. Then, 20 mL of BPB was added. Portions of the 50 mL reaction mixture were withdrawn at various time intervals by means of a long-needle syringe.

Each of the polymer samples was purified by removing the volatile products under vacuum (~ 1 mmHg) at 80°C for 0.5 h, then dissolving in 100 mL benzene and washing with aqueous solution of K₂CO₃ and distilled water repeatedly until base-free. Finally, the bulk of benzene was completely driven off by rotary evaporation and pumping under vacuum. Despite this rigorous treatment, it by no means effected any loss of allylic monomers. The polymers thus obtained were poly(allyl palmitate) (PALPMT), poly(allyl epoxystearate) (PEPALST), and polymer of EPALEPOL (PEPALEPOL). In addition, ALEPOL was also polymerized likewise with the result addressed later. As noted, all polymers prepared contain certain amounts of unreacted allyl esters.

Characterization

The iodine values, i , is a measure of the degree of unsaturation and is expressed in terms of wt % iodine absorbed. Determinations of i and % oxirane were carried out according to the AOCS methods.^{13,14} However, a standing period of 1 h instead of 0.5 h was applied for the former.

GC analysis was taken on a Hewlett Packard 5890 series II and 5790A GC, using the appropriate columns. Refractive index at 30.0°C, n , was determined by an ABBE refractometer. ¹H-NMR and ¹³C-NMR spectra of allyl esters and their polymers in CDCl₃ (Sigma, 99.8 atom % D) were recorded using a JEOL-FX 100 FT-NMR spectrometer, whereas the IR spectra were recorded with a Perkin-Elmer FT spectrophotometer using thin films cast on NaCl windows.

Measurements of specific viscosity, η_{sp} , were performed with an Ubbelohde viscometer at 30.0 ± 0.1°C. Toluene was used as solvent unless otherwise specified. The intrinsic viscosity, $[\eta] = \eta_{sp}/C$, where C is the concentration of the monomer in g/dL.¹⁵ However, for the solutions of the polymers, we resorted to the Schulz-Blaschke equation¹⁶ given by

$$1/C = k_s[\eta] + [\eta]/\eta_{sp} \quad (1)$$

where k_s is an empirical constant. Hence, a linear plot of $1/C$ against $1/\eta_{sp}$ yields the $[\eta]$ from the slope.

The M_n and polydispersity, Δ , were determined by gel permeation chromatography (GPC) using polystyrene standards covering a wide range of molecular weights from 580–3 × 10⁶.

The thermal analyses were performed with a Perkin-Elmer differential scanning calorimeter (DSC-2C) equipped with liquid N₂ subambient cooling accessory and with helium as purge gas.¹⁷ The instrument was calibrated against indium and cyclohexane standards. The sample encapsulated in a standard aluminum pan was annealed at 400 K for 5 min before it was quenched to 170 K, where the heating was commenced with a rate of 20 K/min. The DSC traces were analyzed by a Thermal Analysis Data Station (TADS) standard program.

RESULTS AND DISCUSSION

Figure 1 displays the IR spectra of ALPMT and its polymerization mixtures. In Figure 1(A), the absorption peaks due to the unsaturated carbons are

designated as "a" at 3086 cm⁻¹ for the olefinic =C—H stretch, "b" at 1650 cm⁻¹ for the C=C stretch, and "c" and "d" at 990 and 930 cm⁻¹, respectively, for the terminal C=CH₂ out-of-plane bend. It is noted that the intensities of these absorptions indeed decrease progressively with reaction time, t , indicating the reduction of the number of C=C bonds as the polymerization proceeds. Basically, the same characteristic features were observed in the IR spectra recorded for the other two epoxidized esters and their polymerization products, and, hence, they are not shown herein. However, the situation is rather different in the polymerization of ALEPOL, which only results in the IR spectra resembling Figure 1(A). This means that the allylic absorptions were not dampened in any case. In addition, there were no significant variations in the data of i (= 129.06) and n (= 1.4503) recorded for ALEPOL and its reaction products. All these results indicate that no discernible amount of ALEPOL has been polymerized and that most probably the polymerization has a long induction period. As such, no further investigations were performed on this particular ester. In fact, the foregoing finding is in line with the work of Harrison and Wheeler, who have found that the polymerization of allyl esters can be markedly retarded by the increasing degree of unsaturation in the esters.⁵

The ¹H-NMR spectra obtained from the polymerization of EPALEPOL are shown in Figure 2, where the assignment of each absorption is also given. Clearly, the disappearance of signals a , b , and c and the shifting of resonance d upfield to d' in spectrum B indicate the formation of polymer. Essentially, the same spectra (not shown) were recorded for the polymerization of EPALST. As expected, the ¹H-NMR spectra (not shown) for ALPMT and its polymer may also be represented by Figure 2, except that they do not exhibit resonances i , h and g , j .

The foregoing observations are further confirmed by the ¹³C-NMR spectra of the three systems. Figure 3 illustrates typically one of them. Interestingly, the ¹³C-NMR spectra of the polymerization mixtures of EPALST and EPALEPOL reveal that the oxirane unit remains virtually intact during polymerization. The average value of % oxirane for the former is 5.08 and that for the latter is 2.28, with their respective standard deviations equal to 0.09 and 0.07, based on a total of 10 samples collected over a period of reaction times varying from 0 to 10 h. Indeed, these results are consistent.

More importantly, both the ¹H- and ¹³C-NMR spectra cited above suggest that the amounts of the

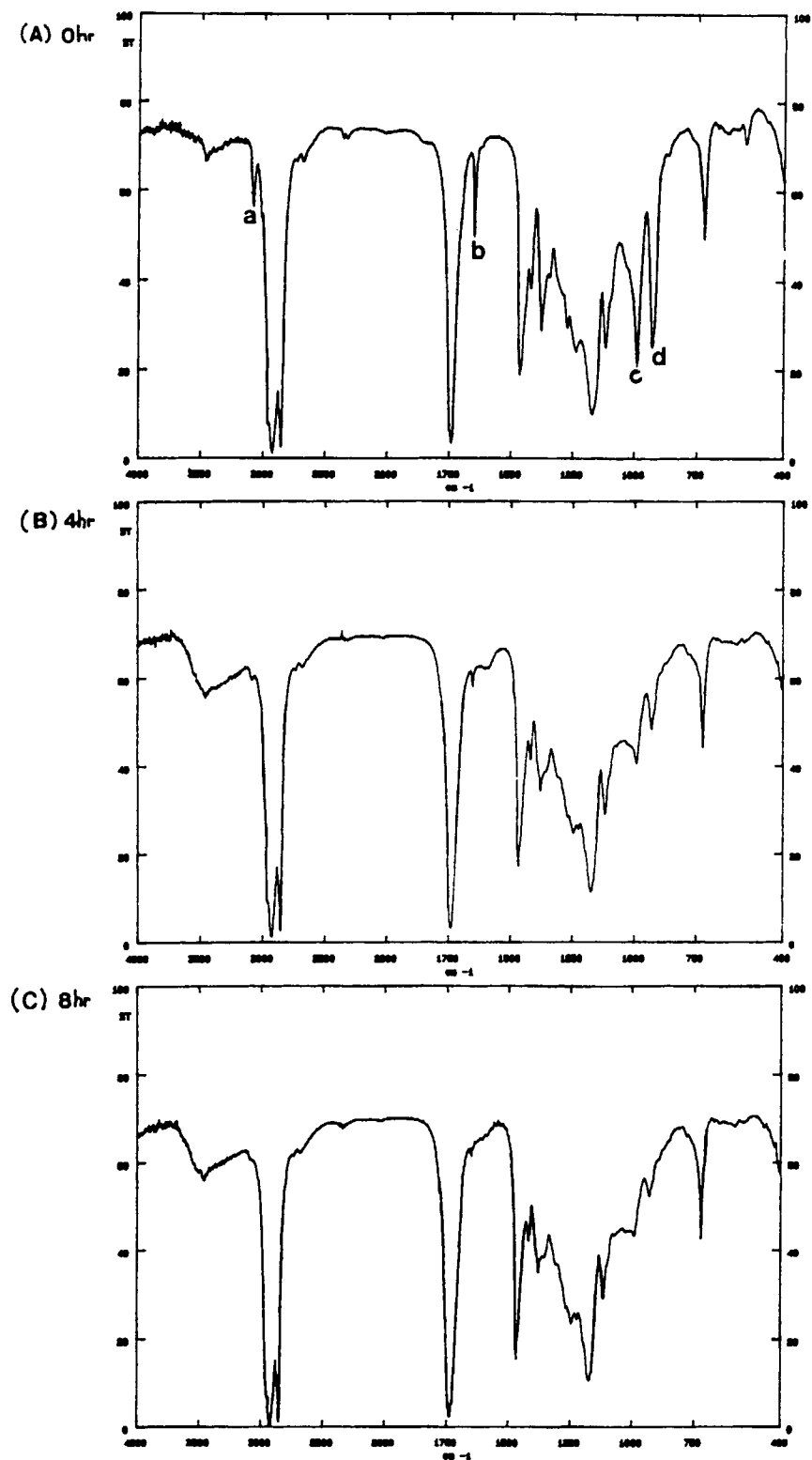


Figure 1 IR spectra of (A) allyl palmitate [$\text{CH}_2\text{CHCH}_2\text{OOC}(\text{CH}_2)_{14}\text{CH}_3$] and after polymerization times of (B) 4 h, and (C) 8 h.

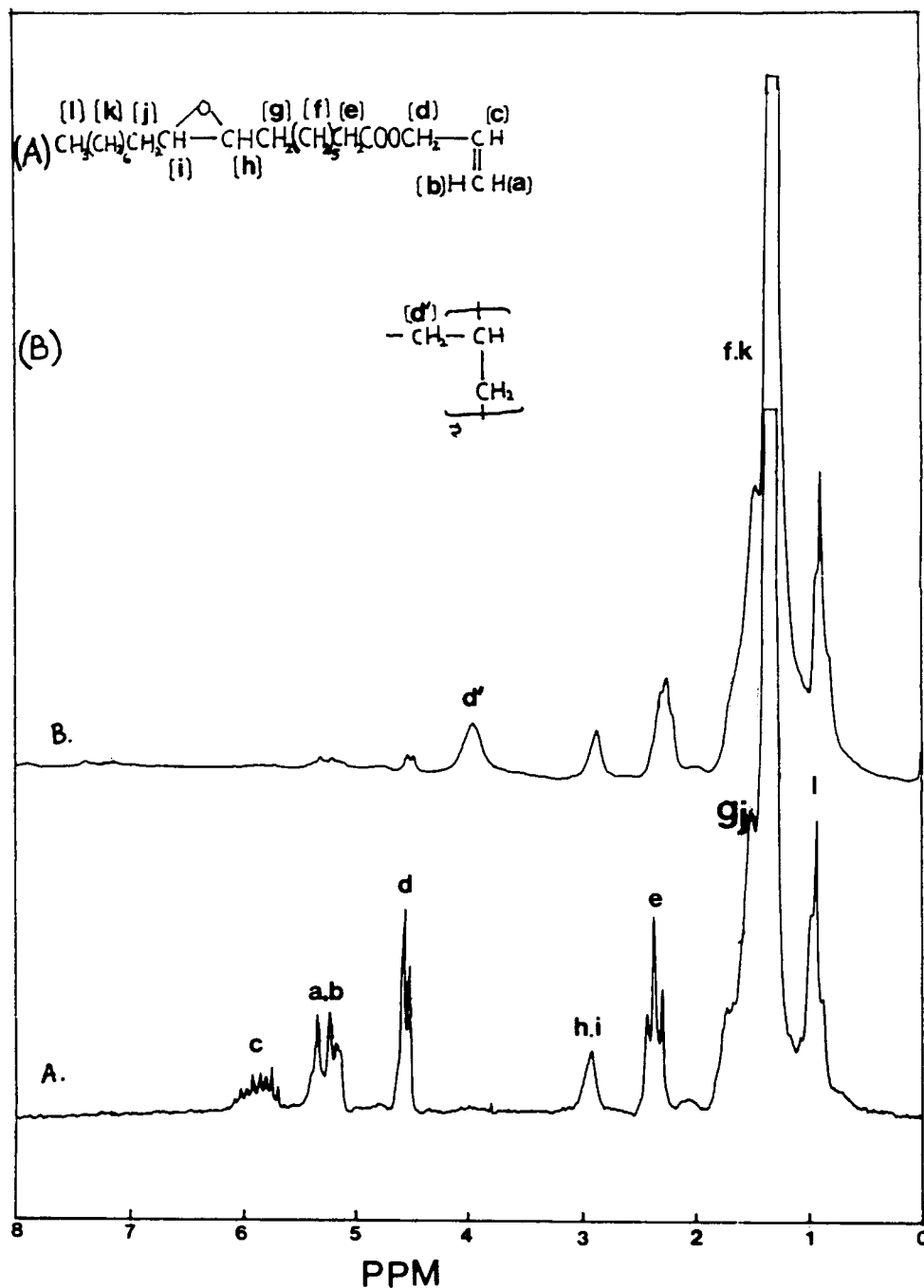


Figure 2 $^1\text{H-NMR}$ spectra of (A) epoxidized allyl ester of palm olein and (B) after polymerization time of 8 h. All are in CDCl_3 .

terminal $-\text{C}=\text{CH}_2$ group present in the polymers are negligibly small. Hence, one could compute the extent of polymerization, p , by $p = (i_0 - i)/i_0$, where i_0 and i are the i 's at $t = 0$ and t , respectively. The i_0 for ALPMT, EPALST, and EPALEPOL are found to be 87.95, 78.56, and 81.24, respectively. Figure 4 shows the kinetic data thus obtained for

the polymerizations of allyl esters by plotting p against t .

One of the distinct features of the polymerization of allyl esters is the linear relationship between the amount of the ester polymerized and the amount of the initiator decomposed at all times for the low concentration of initiator.^{2,18} This means

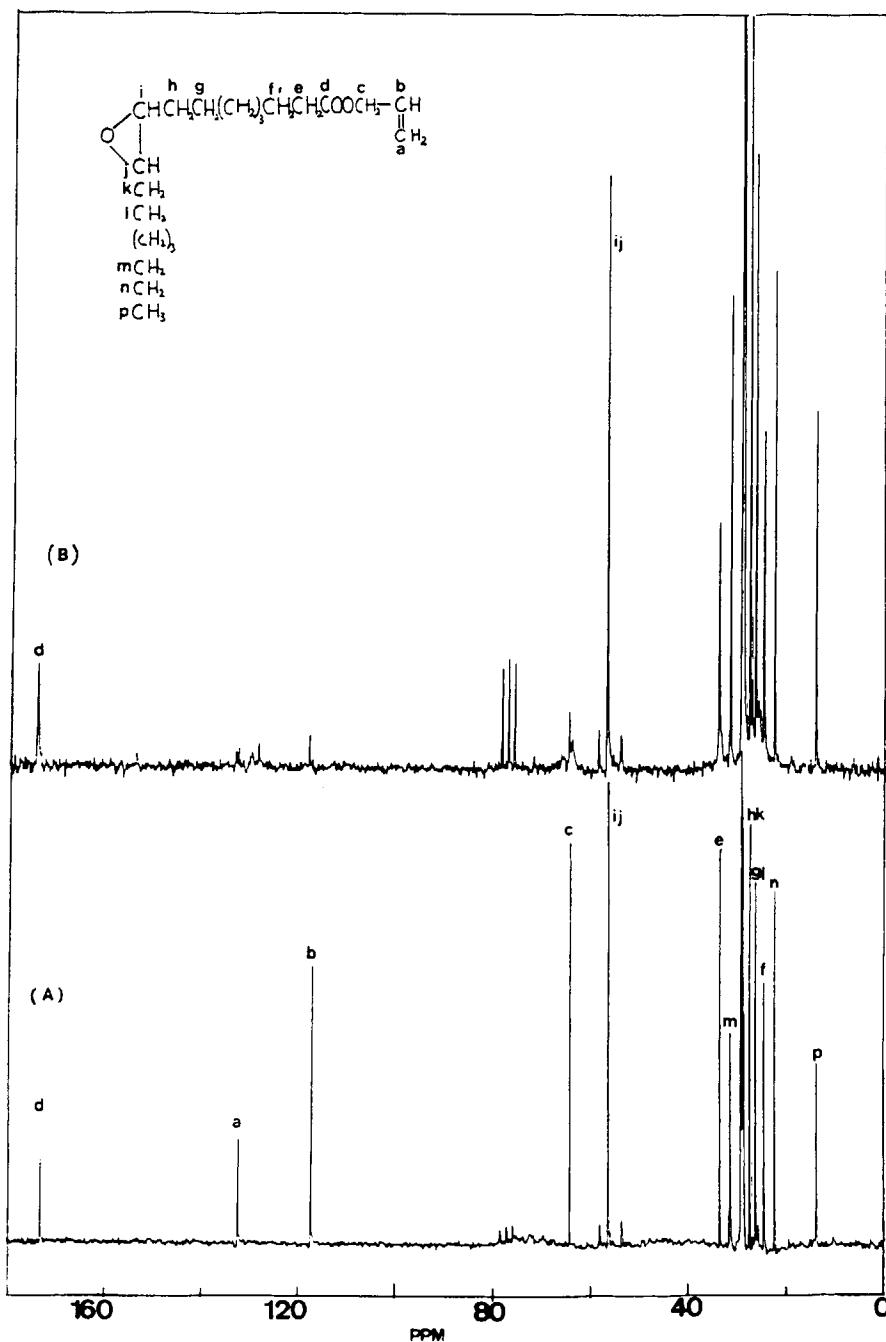


Figure 3 ¹³C-NMR spectra of (A) allyl epoxystearate and (B) after polymerization time of 6 h. All are in CDCl₃.

$$\frac{d[M]}{d[I]} = K \quad (2)$$

where $[M]$ and $[I]$ are the concentrations of the monomer and initiator, respectively, and K is an empirical constant relating to the rate constants of the individual processes proposed.¹⁹ The thermal

decomposition of initiator may be adequately described by an exponential function:

$$[I] = [I]_0 \exp(-k_d t) \quad (3)$$

where the subscript "0" refers hereafter to the time $t = 0$, and k_d is the rate constant. Combining eqs. (2) and (3) yields

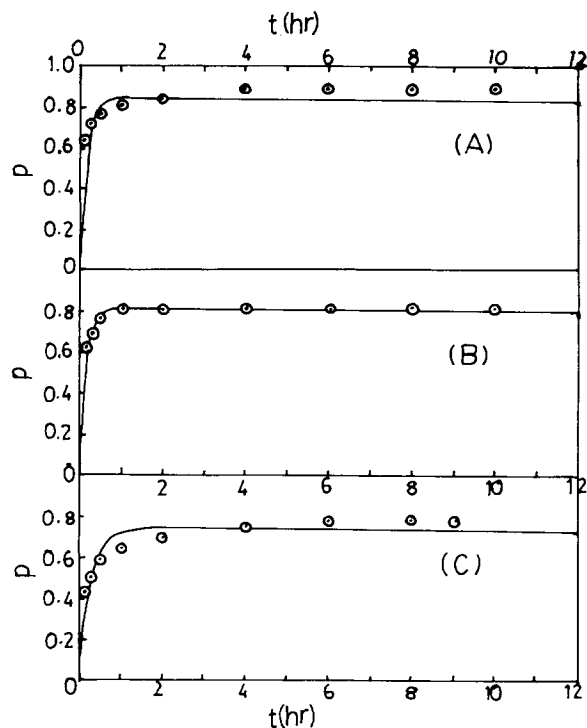


Figure 4 Plot of extent of polymerization, P , against polymerization time, t , for the polymerizations of (A) allyl palmitate, $k_d = 2 \times 10^{-3} \text{ s}^{-1}$, $P_\infty = 0.85$, (B) allyl epoxy-stearate, $k_d = 2 \times 10^{-3} \text{ s}^{-1}$, $P_\infty = 0.82$, and (C) epoxidized allyl ester of palm olein, $k_d = 1 \times 10^{-3} \text{ s}^{-1}$, $P_\infty = 0.76$.

$$P = P_\infty [1 - \exp(-k_d t)] \quad (4)$$

where p is defined by $([M]_0 - [M])/[M]_0$, and P_∞ is the limiting P at $t = \infty$ and is given by

$$P_\infty = K[I]_0/[M]_0 \quad (5)$$

In Figure 4, the curves are drawn according to eq. (4) on the basis of the values of k_d and P_∞ indicated. They fit to the data points satisfactorily with the deviations of estimate on p equal to 0.067, 0.051, and 0.073 for the polymerizations of ALPMT, EPALST, and EPALEPOL, respectively. The k_d for BPB at 120°C obtained by extrapolation from the reported data is $1.9 \times 10^{-3} \text{ s}^{-1}$,²⁰ which is in good accord with the k_d values cited in Figure 4.

The foregoing polymerizations indeed proceed with a rapid rate and are virtually complete in about 2 h, as illustrated in Figure 4. In contrast, Swern and Jordan⁴ found that long-chain allyl esters including ALPMT and allyl stearate display little tendency to polymerize in the presence of benzoyl peroxide. Apparently, the initial rates of polymerization ($= k_d P_\infty$) of ALPMT, EPALST, and EPALEPOL

are observed to be decreasing in that order. Figure 5 demonstrates the parallel behavior for the last two systems in terms of the increasing of n with increasing t .

The viscosity-average molecular weight, M_v , is related to the $[\eta]$ by Mark-Houwink-Sakurada equation. It has been well established that the polymer is under the theta conditions if its M_v is less than its critical molecular weight, M_c .²¹⁻²³ This means that $[\eta]$ is independent of the solvents and is given by

$$[\eta] = K_\theta M_v^{1/2} \quad (6)$$

where K_θ is the unperturbed parameter. The results on the $[\eta]$ of monomer designated by $[\eta]_m$ have been achieved, i.e., $[\eta]_m = 1.73 \pm 0.02$, 2.07 ± 0.12 , and $2.25 \pm 0.09 \text{ mL/g}$ for ALPMT, EPALST, and EPALEPOL, respectively. Equation (6) furnishes their respective $K_\theta = 0.10$, 0.11 , and 0.13 mL/g .

To validate eq. (6) for the present analysis, a number of six solvents with solubility parameters varying from 16.7 to 20.0 $(\text{J/ml})^{1/2}$ has been employed in the $[\eta]$ measurements of a sample collected after 10 h of the polymerization of ALPMT. The results obtained using carbon tetrachloride, chlorobenzene, cyclohexane, cyclohexanone, methyl isopropyl ketone, and toluene as solvents are $[\eta] = 5.66$, 5.46 , 5.46 , 5.38 , 5.47 , and 5.37 mL/g , re-

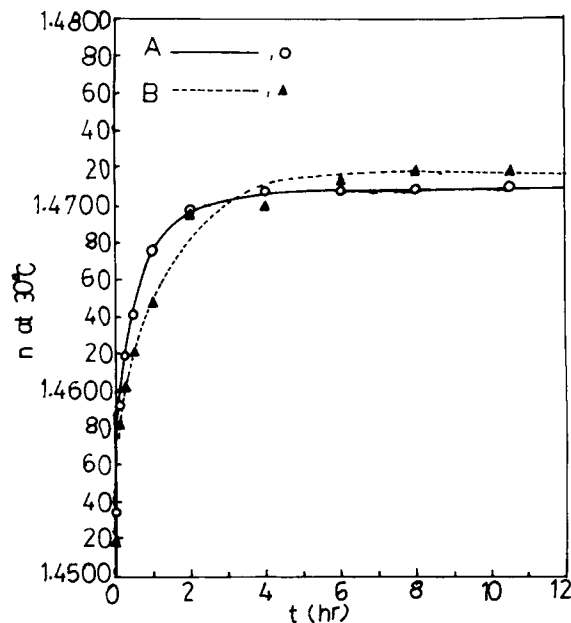


Figure 5 Plots of refractive index at 30°C , n against t for the polymerizations of (A) allyl epoxy-stearate and (B) epoxidized allyl ester of palm olein.

spectively. The average $[\eta]$ is 5.47 ± 0.10 mL/g, indicating that the differences between readings are indeed within the experimental error determined to be $\pm 3\%$ for polymer solutions. Since the polymer sample contains monomer, we propose

$$[\eta] = (1 - p)[\eta]_m + p[\eta]_p \quad (7)$$

which provides a means to estimate the $[\eta]$ of the pure polymer, $[\eta]_p$, corresponding to the extent of polymerization p . Taking $p = 0.90$ [Fig. 4(A)], eqs. (6) and (7) render $[\eta]_p = 5.89$ mL/g and $M_v = 3460$ for PALPMT.

The five samples extracted from the polymerization of EPALST after 2, 4, 6, 8, and 10 h of reaction

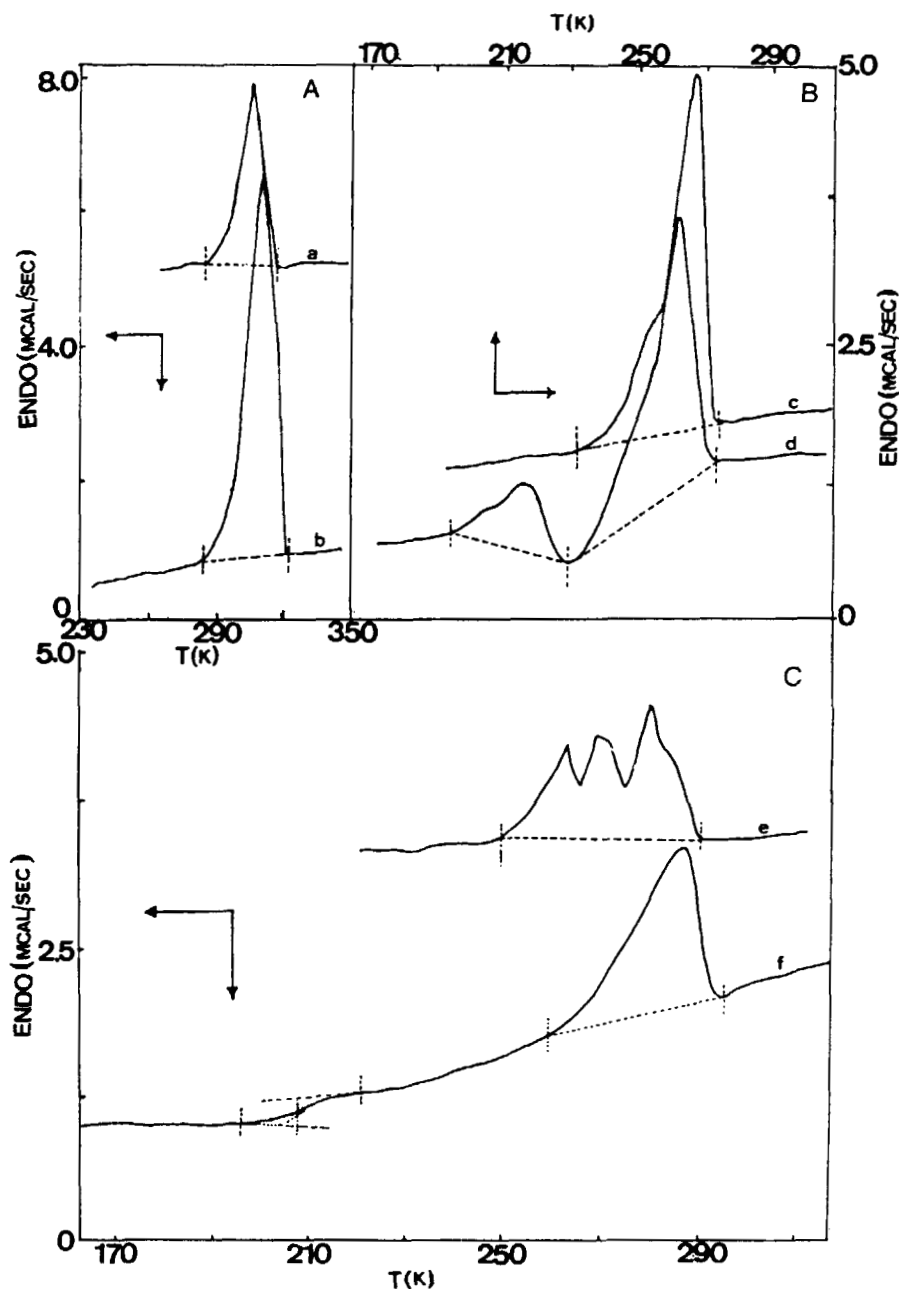


Figure 6 DCS traces of the allyl compounds listed below. The sample sizes are also indicated in parentheses: (a) allyl palmitate (4.42 mg); (b) poly(allyl palmitate) + 10% (w/w) monomer (10.1 mg); (c) allyl epoxystearate (4.22 mg); (d) poly(allyl epoxystearate) + 18% (w/w) monomer (15.7 mg); (e) epoxidized allyl ester of palm olein (3.20 mg); (f) polymer of (e) + (21%) (w/w) monomer (9.40 mg). Heating rate of 20 K/min.

[Fig. 4(B)] were analyzed by the dilute solution viscometry using toluene as solvent. The average $[\eta]$ is 6.63 ± 0.10 mL/g. Following the foregoing estimation scheme, we obtain $[\eta]_p = 7.63$ mL/g and $M_v = 4810$ for the PEPALST at $p = 0.82$. Analogously, the polymerization of EPALEPOL results in $[\eta] = 6.98 \pm 0.23$ mL/g, $[\eta]_p = 8.24$ mL/g, and $M_v = 4020$, on the basis of the last three data points at $p = 0.79$ cited in Figure 4(C).

The M_c of these polymers may be estimated by²⁴

$$K_\theta(M_c \rho_2)^{1/2} = 12.9 \text{ ml/g} \quad (8)$$

where ρ_2 g/mL is the density of the polymer at 25°C. The densities of ALPMT, EPALST, and EPALEPOL have been measured at 30°C to be 0.883, 0.946, and 0.897 g/mL, respectively. Assuming the volume contracts by 10% after polymerization, eq. (8) predicts $M_c \times 10^{-4} = 1.7, 1.3,$ and 1.0 for the PALPMT, PEPALST, and PEPALEPOL, respectively. Clearly, these values are considerably higher than their M_v 's, hence, justifying further the utility of eq. (6) for the present purpose.

The GPC analyses revealed $M_n = 3120, \Delta = 1.23$ for the PALPMT and $M_n = 3150, \Delta = 2.36$ for the PEPALST. However, no GPC data were obtained for the PEPALEPOL because of the nature of the sample. Apparently, the results of dilute-solution viscometry and GPC are compatible in that the ratio M_v/M_n is parallel to Δ . The oligomers reported herein have an average degree of polymerization of 10 ± 1 , which is distinctly lower than that of poly(allyl acetate),⁶ but matches that of poly(allyl erucate) prepared under the same conditions as ours.⁹

The DCS events of the systems of interest are shown in Figure 6, which also furnishes the data presented in Table I. Although the three allylic monomers exhibit melting endotherms of distinct shapes, they have approximately the same molar heat of melting, ΔH_{m1} , equal to 30.2 ± 0.6 kJ/mol (Table I). The ALPMT in Figure 6(A) exhibits a sharper melting peak, indicating that the crystals are more perfect than those formed by the epoxidized allyl esters whose melting behavior is represented by traces c and e. The multiple endotherms observed for EPALEPOL in Figure 6(C) are not unexpected as this modified palm oil fraction is virtually a mixture of a variety of allyl esters with compositions defined previously. However, as the system polymerizes, each growing chain is capable of attacking more than one type of comonomer, resulting in a specific polymer that has a sequence of randomly distributed fatty acid units with different structures and chain lengths. This particular polymer would exhibit a singular melting endotherm as demonstrated by trace f in Figure 6(C). Its crystallinity is rather low and estimated to be 30% on the basis of the ΔH_m values listed in Table I. This is explicable by the fact that copolymerization reduces crystallinity by accepting less comonomer from the crystalline phase.^{25,26} A distinct glass transition temperature, T_g , is observed at 204.4 K due to the existence of its larger amorphous phase. The heat capacity change at T_g , ΔC_p , is 0.42 J/g K, which is in fair agreement with a value of 0.48 J/g K predicted by an empirical relationship between ΔC_p and T_g proposed by Boyer.²⁷

However, the T_g 's of the diluted PALPMT and PEPALST, which are responsible for the traces b

Table I Comparison of Thermal Properties of Allyl Esters and Their Oligomers

Parameter Allyl Compound	T_m (K) ^a (ΔH_m , J/g) ^b	T_g (K) ^c (ΔC_p , J/g K) ^d
a. Allyl palmitate	304.7 (99.6)	—
b. Poly(allyl palmitate) + 10% (w/w) monomer	310.8 (80.8)	—
c. Allyl epoxystearate	266.3 (90.4)	—
d. Poly(allyl epoxystearate) + 18% (w/w) monomer	262.2 (26.8)	—
e. Epoxidized allyl ester of palm olein	217.4 (10.5)	—
	263.1, 269.8	—
	282.1 (94.6)	—
f. Polymer of e + 21% (w/w) monomer	287.3 (27.6)	204.4 (0.42) ^e

^a Maximum of the melting endotherm.

^b Heat of melting obtained by the area under the melting peak.

^c Glass transition temperature recorded as the onset.

^d Heat capacity change at T_g .

^e Estimated by assuming complete crystallization in case e.

and d, respectively, are not detected under the present circumstances. In fact, the former is a highly crystalline polymer estimated to have > 80% crystallinity, whereas the T_g of the latter might have lay hidden in the lower melting peak. Perhaps the most striking feature of Figure 6 is the eutectic temperature at 217.4 K demonstrated by the PEPALST-EPALST combination (trace d).

The melting point, T_m , of the unplasticized polymer designated by T_{m2} may be computed by the Flory-Huggin's theory of polymer solution leading to²⁸

$$\frac{1}{T_{m2}^0} - \frac{1}{T_{m2}} = \frac{R}{\Delta H_{m2} X_n} [\ln(1 - V_1) - V_1(X_n - 1) + X_n \chi V_1^2] \quad (9)$$

where T_{m2} is the T_m of the polymer solution with volume fraction of solvent V_1 ; X_n , the number-average degree of polymerization; R , the gas constant; χ , the polymer-solvent interaction parameter; and ΔH_{m2} , the heat of melting per molar repeat unit. Assuming $\chi = \frac{1}{2}$, $X_n = 10$, $\Delta H_{m2} = \Delta H_{m1}$ and $\rho_1 = \rho_2$, where ρ_1 is the density of the solvent, one estimates the depression of T_m ($= T_{m2}^0 - T_{m2}$) to be ~ 2 K per 10% diluent. Hence, the effects of the unreacted monomers on the T_{m2} determinations are indeed minor, considering their concentrations and experimental errors. In addition, the problem can be readily minimized by manipulating the experimental parameters in eq. (5) such that a high conversion with P_∞ approaching unity is achieved conveniently.

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