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Development of a new method for synthesis of poly(vinyl oleate) from poly(vinyl alcohol)

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Poly(vinyl alcohol) (PVA) can be dissolved in a nonaqueous medium in presence of catalytic concentration of $C_2H_5ONO_2$.DMSO (EN.DMSO). We report the preparation of poly(vinyl oleate) (PVO) by acid-catalysed homogeneous esterification of PVA with oleic acid in a nonaqueous medium. The formation of the ester was confirmed by i.r. and ^{1}H-n.m.r. spectra. The molecular weight of the polymer was determined by g.p.c. and intrinsic viscosity, η was determined by a viscometric method. The glass transition temperature (T_g) and other kinetic parameters were measured from differential scanning calorimetric (d.s.c.) thermograms. Thermal stabilities were checked by thermogravimetric analysis (t.g.a.) and differential thermogravimetric (d.t.g.). A possible mechanism of three-step thermal decomposition of PVO is proposed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: homogeneous esterification; poly(vinyl alcohol); poly(vinyl oleate); ethyl nitrate.DMSO)

INTRODUCTION

Water is practically the only solvent in which PVA can be dissolved. Therefore, some important derivatives, such as esters, acetals of PVA are generally prepared in aqueous medium[1-5]. Poly(vinyl ester)s are prepared industrially, either by the polymerization of vinyl esters or by the transvinylation method[6-10]. Because of this dissolution problem with PVA, esters of fatty acids cannot be prepared from it. We have solved this problem and identified a catalyst, $C_2H_5ONO_2$.DMSO (EN.DMSO) which helps PVA to dissolve in an organic solvent or a mixed solvent. From the solution PVO was prepared by acid-catalysed homogeneous esterification of PVA with oleic acid. The ester was characterized by i.r. study, ^{1}H-n.m.r. study, g.p.c., viscometry, t.g.a., d.t.g., d.s.c. and by other analytical methods.

EXPERIMENTAL

Materials

PVA, white crystalline form (BDH reagent grade; $\overline{DP} = 900$). Oleic acid (BDH reagent grade), dimethyl formamide, DMF (BDH reagent grade), benzene (BDH reagent grade), and dimethyl sulfoxide, DMSO (BDH reagent grade) purified by literature method were used. Acrylic acid (BDH reagent grade) was purified according to the procedure adopted by O'Neil[11]. Paratoluene sulfonic acid, PTSA (BDH reagent grade) was recrystallized from benzene. Nitric acid (BDH reagent grade) and hydrogen peroxide were analytical grade and used without further purification. EN.DMSO was prepared by interaction of acrylic acid with concentrated HNO_3 in DMSO. Purified 7.20 g (0.10 mol) of acrylic acid was mixed with 7.56 g (0.12 mol) of concentrated nitric acid in 100 cm^3 of DMSO. The mixture was then kept at 50°C for about 30 min. The mixture was cooled to room temperature and then treated slowly with 30% H_2O_2 (v/v). A brisk evolution of gases took place. One of the gases was CO_2, as analysed by analytical and i.r. methods. The mixture was then placed in a bath of ice cold water for rapid cooling. When turbid, the mixture was removed and kept at room temperature 25°C overnight. A needle-shaped white crystalline product crystallized out. This was purified by recrystallization several times from acetone and stored over anhydrous calcium chloride.

By microanalysis the elements present in EN.DMSO were found as

Experimental: C = 28.39%, H = 6.47%, N = 8.27%, S = 18.91%
Calculated: C = 28.40%, H = 6.50%, N = 8.28%, S = 18.93%

The melting point of the compound was found to be 150°C. The compound was characterized by i.r. and ^{1}H-n.m.r. techniques.

Methods

The i.r. of PVO was recorded in the region between 4000 cm^{-1} and 200 cm^{-1} with a Perkin–Elmer Spectrophotometer, using thin film of the polymer. The proton n.m.r. was recorded with a WH-270 n.m.r. Spectrometer using DMSO as a solvent. Molecular weight was determined by g.p.c. method with a Waters GPC-150C instrument using THF as the solvent. Intrinsic viscosity $[\eta]$ was determined at 30°C by Ubbelohde viscometer using DMF as the solvent. The percentage of the unconverted hydroxyl groups in the ester was estimated by the acetylation method[12].

D.s.c. was traced by Perkin–Elmer DSC-7 kinetic

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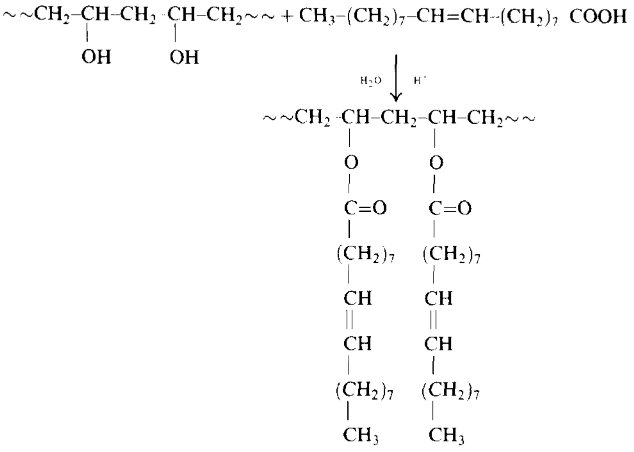
software in air at a scanning rate of 10°C min^{-1}. The kinetic parameters, such as activation energy, order of reaction and rate constant of melting were evaluated by the Freeman and Carroll method[13] from the d.s.c. endotherm. T.g.a. and d.t.g. were performed using a Perkin–Elmer thermal analyser in air at a heating rate of 10°C min^{-1} using 5 ± 1 mg samples.

RESULTS AND DISCUSSION

Preparation of PVO

PVA (4.4 g, 0.10 mol, based on $-CH_2-CHOH-$ as the repeat unit) was dissolved in 150 cm^3 of a solvent mixture of DMF and benzene (4:1, v/v) in presence of EN.DMSO at 60°C in a round-bottom flask. The molar ratio of PVA to EN.DMSO was maintained at $1/1.4 \times 10^{-3}$. Oleic acid 31.07 g (0.11 mol) in 100 cm^3 DMF, was then added slowly to the PVA solution. Homogeneous esterification was carried out by heating the reaction mixture for about 24 h at a temperature around 90°C. The water produced during reaction was removed from the reaction medium as it was formed using the Dean and Stark Principle[14]. After completion of the reaction the solvent was removed by distilling under vacuum. The ester was precipitated by pouring into a mixed solvent of acetone and petroleum ether (1/2 by volume), four times in volume of the ester solution with constant stirring. Reprecipitation was carried out twice to ensure the complete removal of unreacted PVA and oleic acid. To remove PTSA and the last trace of other impurities the ester was washed with benzene and dried at 40°C and stored over anhydrous calcium chloride. The conversion to ester was nearly 75–80%.

It is proposed that the following reaction may take place between PVA and oleic acid for the production of PVO.



$$\sim\sim CH_2-\underset{OH}{CH}-CH_2-\underset{OH}{CH}-CH_2\sim\sim + CH_3-(CH_2)_7-CH=CH-(CH_2)_7\,COOH \xrightarrow[H_2O]{H^+} \sim\sim CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ (CH_2)_7\\ |\\ CH\\ \|\\ CH\\ |\\ (CH_2)_7\\ |\\ CH_3}}{CH}-CH_2-\underset{\substack{|\\ O\\ |\\ C=O\\ |\\ (CH_2)_7\\ |\\ CH\\ \|\\ CH\\ |\\ (CH_2)_7\\ |\\ CH_3}}{CH}-CH_2\sim\sim$$

The i.r. spectrum of PVA showed some interesting changes when reacted with carboxylic acid. On esterification, the O–H stretching vibration bands weakened and shifted towards higher frequencies owing to cleavage of polymeric hydrogen bond chain[15]. The i.r. spectrum of PVO is presented in *Figure 1*. According to Hummel and his coworkers[16] infra-red spectra of aliphatic polyesters can be divided into four ranges, between 3000 cm^{-1} and 2800 cm^{-1}, 1760 cm^{-1} and 1710 cm^{-1}, 1500 cm^{-1} and 1100 cm^{-1} and 1100 cm^{-1} and 720 cm^{-1}. Our results tally

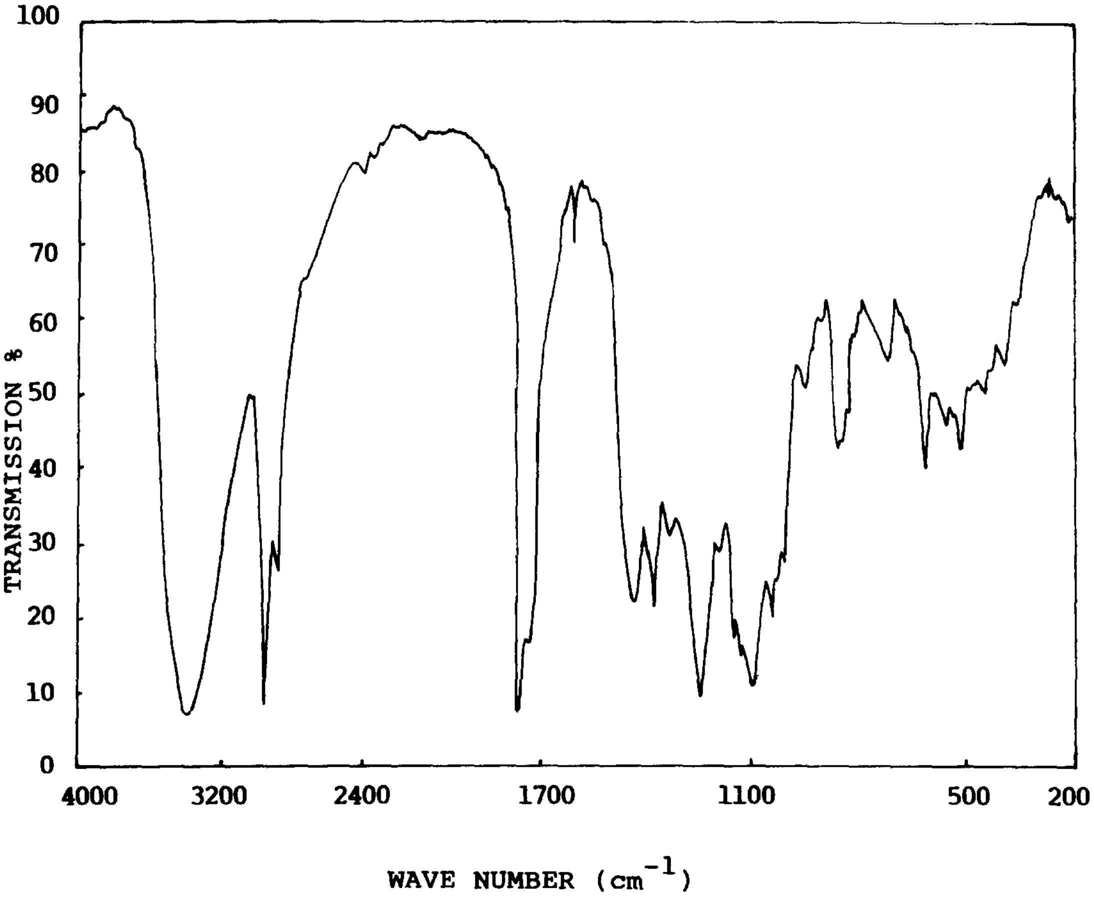


Figure 1 The i.r. spectra of PVO (in thin film)

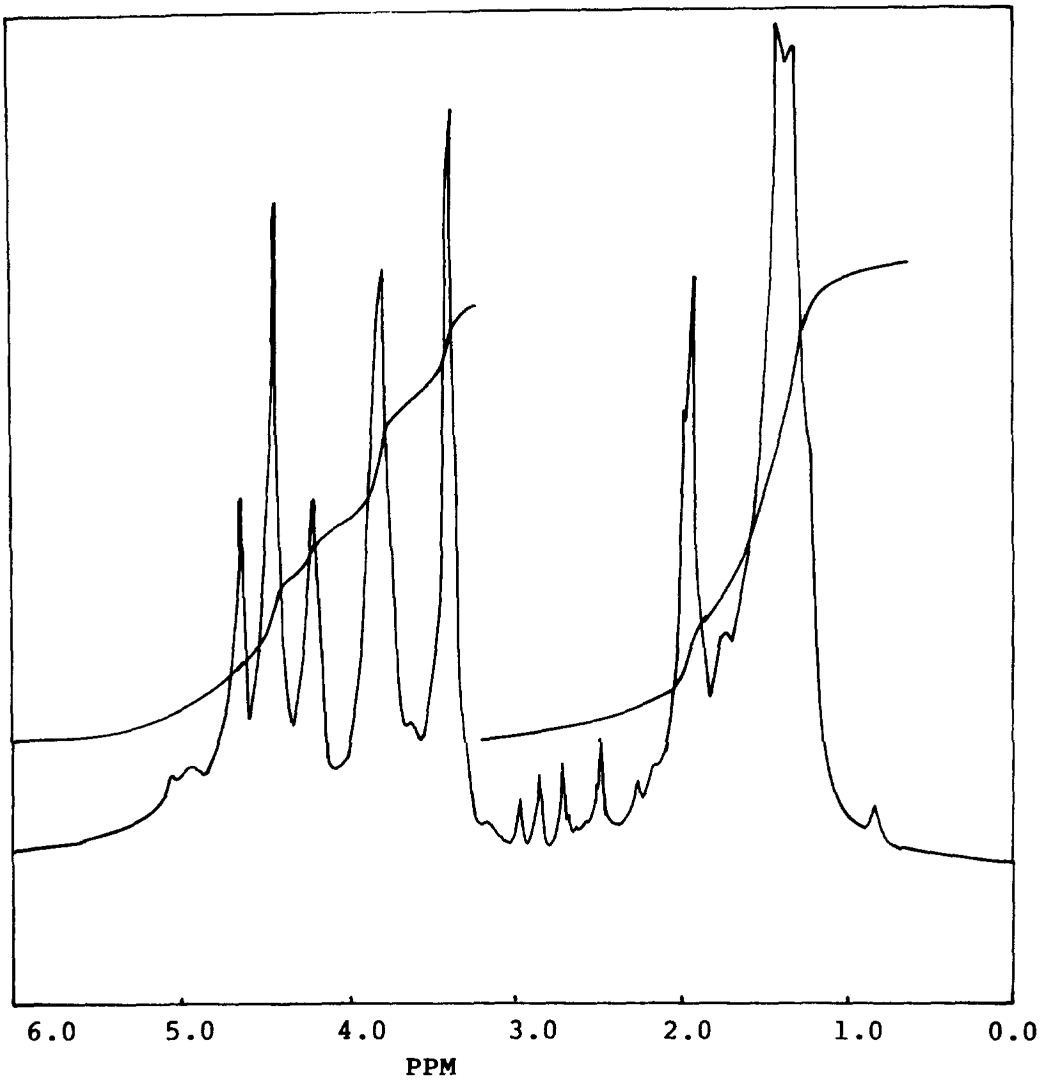


Figure 2 The ^{1}H-n.m.r. spectrum of PVO (in DMSO)

with the results of Hummel and co-workers and also other authors[17]. The following assignment can be made. The band between 2940 cm^{-1} and 2870 cm^{-1} results from the antisymmetric stretching vibrations of the methylene groups together with the symmetric one. The bands at 1745 cm^{-1} are due to the carboxyl group (C=O). The third range between 1500 cm^{-1} and 1100 cm^{-1} belong mainly to wagging vibration of the methylene group and to the C–O–C and C–C stretching vibration. The fourth band, between 1100 cm^{-1} and 720 cm^{-1}, belongs to rocking vibrations of the methylene groups and also chain-stretching vibrations involving the ester groups. A weak band is observed at 1610 cm^{-1} for the C=C.

A typical ^{1}H-n.m.r. spectrum for PVO is shown in *Figure 2*. The signals observed at 0.83, 1.3–1.9 and 4.2–4.4 ppm are due to methyl ($-CH_3$), methylene ($-CH_2-$) and methine ($-\underset{|}{C}H-$) protons respectively[18,19]. The signals at 4.9 ppm, is due to the olefinic protons ($-CH=CH-$), confirmed the formation of the ester.

From g.p.c. analysis the weight average molecular weight (M_w) of the ester was found to be 129 000. Intrinsic viscosity $[\eta]$ of the polymer was obtained as 1.42 dl g^{-1}.

The percentage of unconverted hydroxyl groups in the ester was estimated by the acetylation method. The results indicated that about 60% of the hydroxyl group of PVA had been converted to ester groups. The PVO was soluble in a number of organic solvents such as DMF, DMSO, dioxane, C_2H_5OH, THF, $CHCl_3$, CH_3COOH, CH_3OH etc. The melting point of PVO was 185°C.

A typical d.s.c. thermogram for PVO is shown in *Figure 3*. From the d.s.c. studies the glass transition temperature, T_g, was found to be 53°C. The activation energy, E, of melting was 62.43 ± 1.34 kJ mol^{-1}. The order of melting reaction of the ester was calculated as $n = 1.02 \pm 0.02$. The rate constant, k, was found to be $7.57 \times 10^6 \pm 3.81$.

To check the thermal stability of the ester the t.g.a. and d.t.g. curves (*Figure 4*) were recorded in air. From d.t.g. curves it was observed that the ester decomposed in three stages[20]. The decomposition temperatures were determined by the intersection of the tangent to the steepest part of the t.g.a. curve with its strain-line. It was found that PVA decomposed by the loss of water from two adjacent hydroxyl groups at temperatures above 150°C[21]. This was the first stage degradation, in which H_2O was removed from neighbouring pairs of unconverted hydroxyl groups of the ester. The initial decomposition temperature (IDT_1) for the first stage of the PVO was 280°C. The second stage decomposition

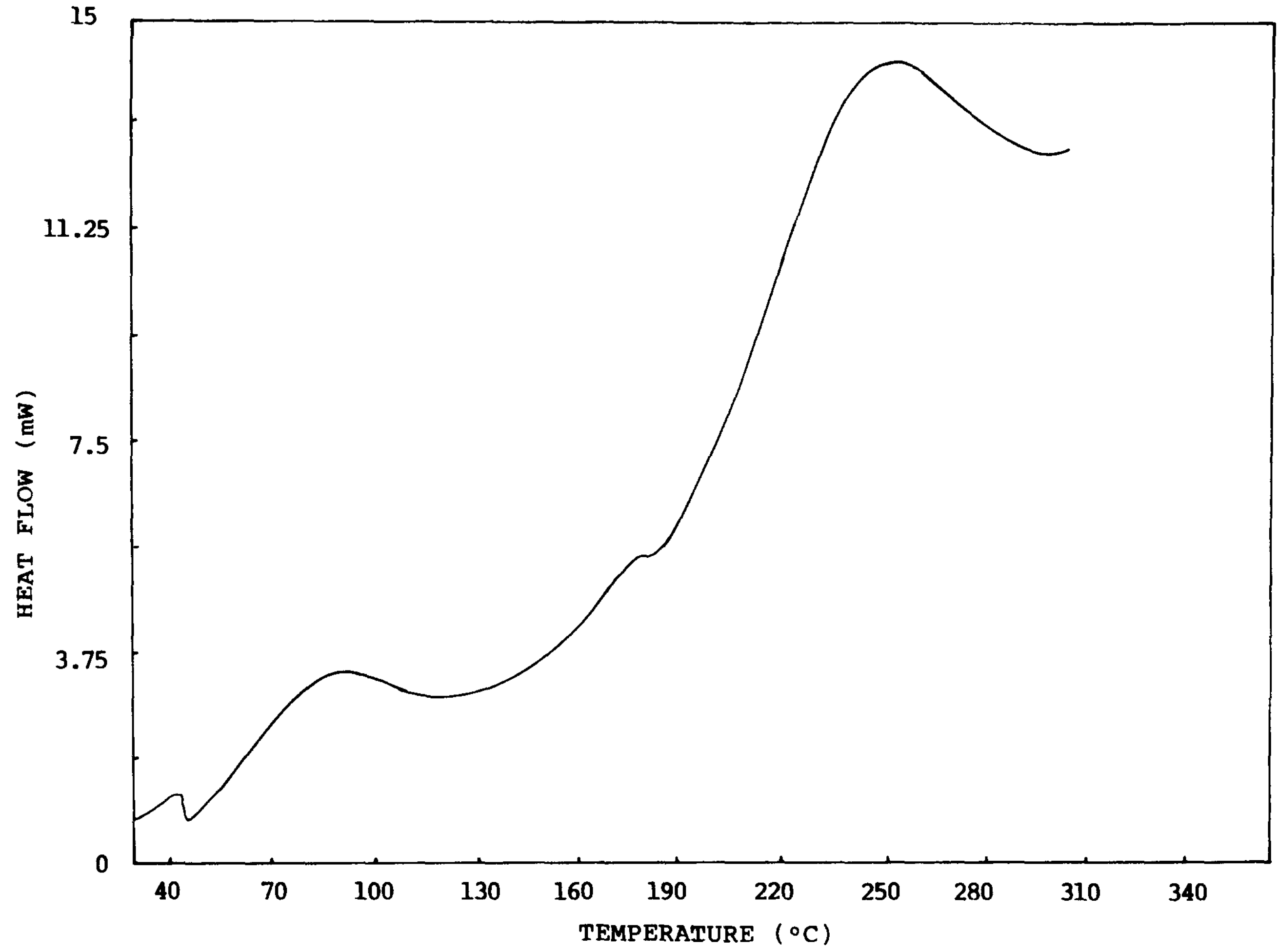


Figure 3 D.s.c. curve of PVO

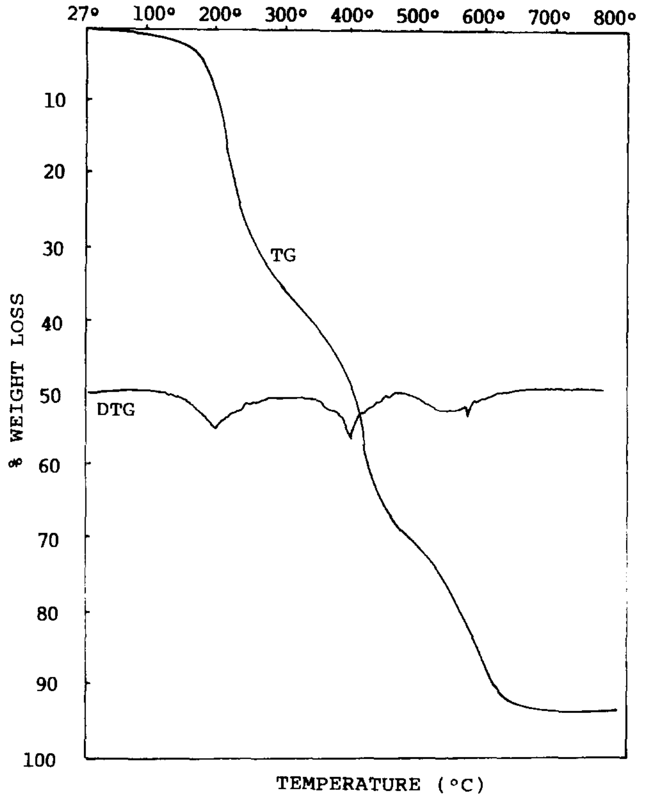


Figure 4 T.g.a. and d.t.g. curves of PVO in air at a heating rate of 10°C min^{-1}

resulted from the removal of CO, CO_2, hydrocarbons, etc.[22-24] from the ester. The initial decomposition temperature (IDT_2) for the second stage of the ester was 455°C. The third stage decomposition was due to the production of carbon at temperatures above 500°C. Integral procedural decomposition temperature (IPDT)[25] was also found, 450°C.

The method may lead to the synthesis and development of polyacetals, polyethers and other commercially important chemicals from PVA. However, 100% conversion of all the hydroxyl groups into oleate groups still eludes us.

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