may be the natural inducer for methylmalonate semialdehyde dehydrogenase in *P. fluorescens* UK-1. However, the possibility that methylmalonate semialdehyde, isobutyrate, 2-oxoisovalerate, or valine are also the inducers of the enzyme is not excluded.

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Low-temperature Transitions of Chlorinated Polyethylenes

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Several studies have been made regarding the low-temperature relaxation behavior of solution chlorinated polyethylenes.[1-4] It has been found by dynamic-mechanical studies that the γ-relaxation process occurs below -100°C in amorphous CPE-polymers. Using dielectric relaxation measurements on CPE with low chlorine content the temperature of maximum loss at a frequency of 1 kHz was about -90°C. The γ-transition of commercial polyethylenes has been reported to occur in two temperature regions, -120 to -130°C and -80 to -90°C.[5] In this study, suspension chlorinated low-density polyethylenes were investigated by differential thermal analysis measurements, DTA, in the temperature range -120° to 0°C.

Experimental. The samples were commercial suspension-chlorinated low-density polyethylenes (CPE) of varying chlorine content. The source of all CPE samples, the parent polymer, was a low-density polyethylene which was also used in these studies. The characteristics of the samples are given elsewhere.[6] The Du Pont 900 DTA apparatus was used for these measurements. The instrument was equipped with a low-temperature chamber made of polypropylene which allowed the measurements to be carried out in the temperature range -120° to 0°C. Liquid nitrogen was used as a cooling medium. The procedure employed in the runs was as follows: A macro sample tube was filled with the powdered polymer as received to depth of 5 mm. The sample was melted, pressed with the ceramic sleeve and the thermocouple was inserted in the softened mass. The reference tube consisted of a thermocouple inserted midway into 5 mm of glass beads. The tubes were placed into the low-temperature chamber. The samples were heated above melting points of the polymers, $+120$°C, to remove internal stresses and then cooled to liquid nitrogen temperature. The heating rate was 20°C/min.

Results and discussion. Thermograms of LDPE and CPE are seen in Fig. 1. The composition and transition points of the polymers are given in Table 1.

It can be seen that the transitions of CPE occur in the temperature intervals -38° to -39°C and -104° to -110°C. The latter range is seemingly related to the γ-transition of CPE. It has been found that the mechanical loss maximum at 2.7 Hz of solution chlorinated CPE with a chlorine content 20–45 % lies in the temperature range immediately below -100°C.[1,2] It has been shown that the γ-transition of semi-crystalline PE arises principally from contributions of the non-crystalline regions of the polymer.[8] On the basis of structural studies suspension chlorinated polyethylene, CPE, can be visualized as containing definite amounts of ethylene ($-CH_2-CH_2-$) and vinyl chloride ($-CH_2-CHCl-$) units when the chlorine content of the polymer varies between 0– and 56 %.[9,10] The distribu-

Table 1. Composition and transition temperatures of polymers.

Sample	Composition [a]	Transition temperature, °C Tg	γ-transition
LDPE		−39	−90
CPE (27.8 % Cl)	$(CH_2CH_2)_{0.697}(CH_2CHCl)_{0.303}$	−39	−110
CPE (35.0 % Cl)	$(CH_2CH_2)_{0.585}(CH_2CHCl)_{0.415}$	−38	−104
CPE (42.8 % Cl)	$(CH_2CH_2)_{0.422}(CH_2CHCl)_{0.578}$	−38	−106

[a] Calculated on the basis of chlorine content.[7]

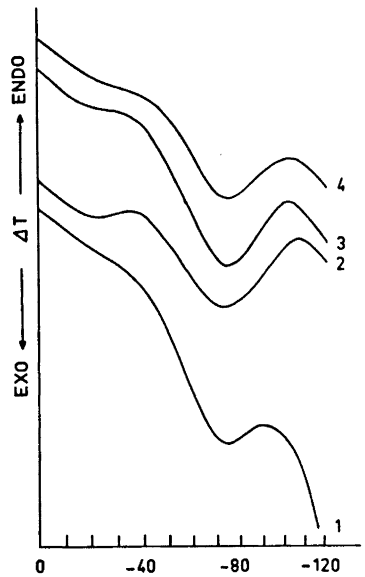

Fig. 1. Thermograms of powdery polymers. 1. LDPE; 2. CPE (27.8 % Cl); 3. CPE (35.0 % Cl); 4. CPE (42.8 % Cl).

tion of chlorines in the CPE chain can be considered as a rather statistically random distribution especially in the early steps of chlorination both in solution and suspension chlorinated polymers.[11] In CPE there are unchlorinated $-CH_2-$ groups and chlorinated segments $-CHCl-$ in amorphous regions which probably take part in thermal motions of γ-process.

The transition of the parent PE corresponds to the glass temperature of low-density polyethylene, -38 ± 5°C, found in adiabatic calorimetric studies [12] and from the extrapolation of Tg data on chlorosulfonated polyethylenes.[13] The occurrence of a transition for suspension chlorinated CPE at the same temperature as for LDPE at low chlorine contents has been demonstrated experimentally. This phenomenon has also been described by considering the Tg of the chlorinated material to be a linear function of the mol fraction of hypothetical homopolymers weighted by their respective Tg's.[14]

Thermograms have also been run on material which had been compression molded into discs between polished steel plates at 160°C at 84 kg/cm². These results were quite different and difficult to reproduce, confirming that properties if these semicrystalline polymers are sensitive to temperature and pressure history.[14]

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The Benzoylation of Some Glycosides with a Mixture of Benzoic Acid, Triphenylphosphine, and Diethyl Azodicarboxylate

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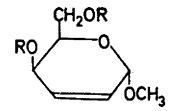
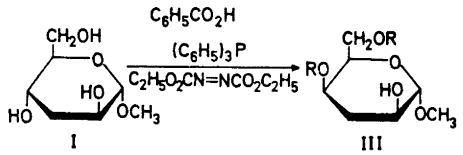
Mitsunobu and Eguchi have described the substitution of alchohols using nucleophiles such as benzoic acid, dibenzyl hydrogen phosphate, and phthalimide in the presence of triphenylphosphine and diethyl azodicarboxylate.[1,2] The reactions lead to products with inverted configuration and are of potential interest in carbohydrate chemistry for the synthesis of phosphorylated sugars, amino sugars, and for the inversion of the configuration at specific positions *via* benzoylation. A preliminary report by Jones and co-workers on the synthesis of some amino sugars using phthalimide,[3] following the procedures outlined by Mitsunobu and Eguchi [1,2] prompts us to report our experiences in attempted inversion reactions using benzoic acid as the nucleophile.

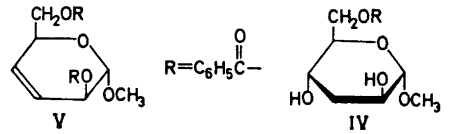
In connection with the synthesis of disaccharide derivatives containing 3,6-dideoxyhexopyranosyl moieties [4–6] it would be of interest to be able to effect the simultaneous inversion of two hydroxyl groups at the 2- and 4-positions in 3-deoxy-D-*arabino*-hexosides. This would give access to 3,6-dideoxy-D-*xylo*-hexosides from the previously synthesized D-*arabino* stereoisomers.[4] As a model for this conversion, methyl 3-deoxy-α-D-*arabino*-hexopyranoside (I) [4,7] was treated with benzoic acid,



II



I III



V IV

triphenylphosphine, and diethyl azodicarboxylate. The reaction mixture was fractionated on silica gel to give methyl 4,6-di-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (II, 23 %) in crystalline form and with physical constants in agreement with literature values,[8] methyl 4,6-di-*O*-benzoyl-3-deoxy-α-D-*lyxo*-hexopyranoside (III, 47 %) and methyl 6-*O*-benzoyl-3-deoxy-α-D-*arabino*-hexopyranoside (IV, 12 %). The dibenzoate III was identified as follows. The NMR indicated the presence of two benzoyl groups. Acetylation afforded a monoacetate (NMR) and debenzoylation of III afforded syrupy methyl 3-deoxy-α-D-*lyxo*-hexopyranoside $[\alpha]_D$ +84° (methanol) (lit.[9] $[\alpha]_D$ +98°). Hydrolysis, conversion into the corresponding 3-deoxy-D-hexitol acetate and examination by GLC-MS showed that the derivative had the MS expected, but retention