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The non-oxidative thermal degradation of poly(di-*n*-alkyl itaconates). I. Analysis of the thermolysis volatiles

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Abstract

The volatiles arising from the thermal degradation of poly(di-*n*-alkyl itaconates) with ester substituents ranging from methyl to *n*-octyl were analysed. The corresponding monomer was found to be the major degradation product. A significant amount of itaconic acid in the volatiles was also found in the case of poly(diethyl itaconate). A detailed mechanism of the thermal degradation of the studied polymers is given.

Keywords: Thermal degradation; Polyitaconates; Volatiles; Mechanism

1. Introduction

Poly(di-itaconates) are structurally similar to poly(methacrylates) in which one of the hydrogens of the methyl group in the side chain of the poly(methacrylate) is substituted by an ester group. Of the poly(methacrylates), the thermal degradation of poly(methyl methacrylate) has been studied the most extensively. Due to structural similarities, it may be expected that a poly(di-itaconate) with the corresponding ester substituent will thermally degrade similarly to a poly(methacrylate) [1–5].

The first investigations of the thermal stability of poly(mono- and di-*n*-alkyl itaconates) were performed by Cowie and Haq [6]. Further work on the thermal degradation of poly(dimethyl itaconate) was done by Veličković and Popović [7]. The thermal degradation kinetics of poly(di-*n*-alkyl itaconates) were studied by Popović et al. [8,9]. These investigations established that poly(di-*n*-alkyl itaconates) predominantly depolymerised. The goal of this study was to determine the detailed non-oxidative thermal degradation mechanism of poly(di-*n*-alkyl itaconates) with the ester group ranging from methyl to the *n*-octyl group, by analysing the condensable and non-condensable thermolysis volatiles.

2. Experimental

2.1. Monomers

Dimethyl itaconate (DMI) (Aldrich, p.a.) was recrystallised twice from methanol (Merck, p.a.) before further use. Diethyl- (DEI), di-*n*-butyl- (DBI), di-*n*-hexyl- (DHI) and di-*n*-octyl itaconate (DOI) were synthesised by esterifying itaconic acid (Merck, p.a.)

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Table 1
Polymerisation conditions and molar masses of the polymers used

Polymer	Polymerisation temperature (°C)	c (AIBN) (mol %)	Yield (%)	$\overline{M}_w$ (LS) (g/mol)	$\overline{M}_w$ (GPC) (g/mol)	$\overline{M}_n$ (GPC) (g/mol)	$\overline{M}_w/\overline{M}_n$ (GPC)
PDMI-1	35	0.5	–	4.21×10^5	4.04×10^5	1.22×10^5	3.3
PDMI-2	40	0.5	–	3.42×10^5	3.31×10^5	0.99×10^5	3.4
PDEI-1	37	0.5	22.1	3.10×10^5	2.93×10^5	1.19×10^5	2.5
PDEI-2	32	0.1	25.5	5.97×10^5	5.72×10^5	2.08×10^5	2.7
PDBI	32	0.1	24.7	8.19×10^5	8.01×10^5	2.88×10^5	2.8
PDHI	32	0.25	30.0	7.71×10^5	7.46×10^5	2.84×10^5	2.6
PDOI	35	0.7	19.6	3.17×10^5	3.08×10^5	1.20×10^5	2.6

with the corresponding *n*-alkyl alcohol (all Aldrich, p.a.). The structures of the monomers were confirmed by IR and ^{1}H NMR spectroscopy. A Perkin Elmer Grating Spectrophotometer 357 was used to record the IR spectra of neat liquids. ^{1}H NMR Spectra were recorded with a Varian T-60 instrument using deuterated chloroform as the solvent. The purity of the monomers was determined by gas chromatography ($\gg$98%). A Perkin Elmer 8500 instrument with a Permaphase PVMS/54 capillary column and FID was used.

2.2. Polymers

The monomers containing α,α'-azobisisobutyronitrile (AIBN) were polymerised in bulk in glass ampoules in the temperature range 30–40 °C. Oxygen was removed from the monomers prior to polymerisation by consecutive freezing/thawing cycles under high vacuum (ca 10^{-5} mbar). The polymerisations were done to yields no greater than 30%. The polymers were purified by multiple dissolution/precipitation in benzene/methanol (both Merck, p.a.).

The average molar masses of the starting polymers, i.e. poly(dimethyl itaconate) (PDMI), poly(diethyl itaconate) (PDEI), poly(di-*n*-butyl itaconate) (PDBI), poly(di-*n*-hexyl itaconate) (PDHI) and poly(di-*n*-octyl itaconate) (PDOI), were determined by light scattering and gel permeation chromatography (GPC) measurements. A Chromatix KMX-6 instrument was used to measure the weight-average molar masses. The values of the refractive index increments, d*n*/d*c*, for the required polymer–solvent–temperature combinations were taken from the literature [10]. A Knauer instrument with three Shodex columns (Shodex GPC A-803, TSK G500 HXL and Ultrastyragel 105 Å), RI detector and a Trilab data processing station were used for the GPC measurements. Poly(methyl methacrylate) (PMMA) (Röhm) standards were used to calibrate the GPC measurements.

2.3. Isothermal degradation

The polymer samples were degraded in a furnace the temperature of which was regulated by a rheostat. The temperature of the furnace, measured by an Ni–NiCd thermocouple, was kept constant to ~1 °C. The experiments were performed in the temperature range 200–320 °C. The polymer samples, of average mass 60 mg, were degraded in glass cells previously degassed to ca 10^{-5} mbar by means of a vacuum turbo pump (Leybold). The cells used were glass tubes of 5 mm internal diameter and 90 mm length with a narrow sidearm of 2 mm internal diameter and 90 mm length immersed in liquid nitrogen during the thermolysis to collect the evolved condensable volatiles. Cells without a sidearm were used in experiments in which non-condensable volatiles were

Table 2
Composition of thermolysis volatiles formed during the thermal degradation of poly(di-*n*-alkyl itaconates) at 280 °C, heating time 30 min, calculated on the basis of GC results with direct sample injection, excluding the cold ring fraction

	Compound[a]	PDMI[b]	PDEI	PDBI	PDHI	PDOI
1 + 2	1-Alkene/*n*-alkane	–	–	–	0.31	0.3
3	*n*-Alkanol	0.59	0.07	0.52	1.27	0.73
4	*n*-Alkyl acetate	0.11	0.09	0.27	0.34	0.43
5	*n*-Alkyl acrylate	0.78	0.53	0.43	0.33	0.37
6	*n*-Alkyl methacrylate	0.22	0.18	0.29	0.16	0.15
7	*n*-Alkyl ester of 3-methylene butyric acid	0.26	0.26	0.24	0.16	0.16
8	Isomer 1 + isomer 2 (mesaconate + citraconate)	1.64	3.13	5.01	6.74	7.20
9	Di-*n*-alkyl itaconate (monomer)	94.22	84.80	89.01	88.73	85.71
10	Di-*n*-alkyl ester of 1-methyl succinic acid	0.19	0.27	0.19	0.52	1.16
11	Itaconic acid	1.99	10.67	4.04	1.45	3.70

[a] The alkyl group is methyl, ethyl, *n*-butyl, *n*-hexyl and *n*-octyl for PDMI, PDEI, PDBI, PDHI and PDOI, respectively.

[b] PDMI sample degraded at 300 °C.