Polymer Degradation and Stability 96 (2011) 1141–1148

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Photo-degradation of poly(neopentyl isophthalate). Part II: Mechanism of cross-linking

Przemyslaw Malanowski [a,b], Rolf A.T.M. van Benthem [a,c,*], Leendert G.J. van der Ven [a], Jozua Laven [a], Srdjan Kisin [a,1], Gijsbertus de With [a]

[a] *Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands*
[c] *DSM Ahead BV, PO Box 18, 6160 MD, Geleen, The Netherlands*

ARTICLE INFO

Article history:
Received 17 January 2011
Accepted 22 February 2011
Available online 9 March 2011

Keywords:
Polyester
Coating
UV exposure
Gel formation
Methanolysis

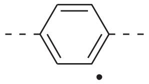
ABSTRACT

The mechanism of cross-linking of poly(neopentyl isophthalate) (PNI) by photo-degradation in nitrogen atmosphere was investigated. The exposure of PNI to UV light resulted in gel (insoluble material) formation. The gel material was collected and the morphology of the gel material was characterized with SEM. The gel has the highest density near the coating surface. To obtain information on the cross-linking at a molecular level the gel was decomposed by methanolysis and the decomposition products were analysed with LC-MS. Besides the expected "grafting" types of cross-links (phenyl-to-phenyl coupling) also "chain coupling" types of cross-links were detected (recombination of neopentyl glycol based moieties). Analysis of samples that had been exposed to UV light in air indicates that the phenyl-to-phenyl coupling also occurs in the presence of oxygen.

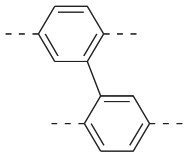
1. Introduction

The exposure of aromatic polyesters to ultra violet (UV) light leads to extensive chemical changes as documented for poly(ethylene terephthalate) [1–4], poly(butylene terephthalate) [5–7] and poly(neopentyl isophthalate) [8,9]. Typically, under the influence of UV irradiation an aromatic ester bond can dissociate in two radicals (photolysis). These radicals can transfer the radical function by abstracting a hydrogen from an adjacent polymer chain, can react with an oxygen molecule (photo-oxidation) or can recombine and form larger molecules (photo-cross-linking). As a first step of this cross-linking process a high molar mass sol fraction (cross-linked molecules, yet still soluble) is formed while more extensive cross-linking leads to gel formation (insoluble material).

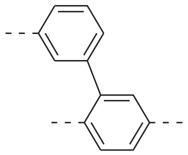
The chemistry of photo-cross-linking of poly(ethylene terephthalate) was investigated by Marcotte et al. Based on ESR (electron spin resonance), they proposed the formation of an intermediate phenyl radical [1]:



The recombination of two of such radicals would lead to the cross-linking of polymer chains:



Later, other researchers referred to this reaction as a possible mechanism of photo-cross-linking of aromatic polyesters. Rivaton [5] studied the photochemistry of poly(butylene terephthalate) with infrared (IR) spectroscopy and suggested the formation of an m-biphenyl structure as an alternative to the above mentioned mechanism of photo-cross-linking.



The previous studies, however, relied mainly on IR spectroscopy. New groups formed by cross-linking, being carbon to carbon

---

* Corresponding author. Laboratory of Materials and Interface Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. Tel.: +31 402472029; fax: +31 402445619.

E-mail address: r.a.t.m.v.benthem@tue.nl (R.A.T.M. van Benthem).

[1] Present address: Dow Europe GmbH, Bachtofelstrasse 3, 8810 Horgen, Switzerland.

0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.02.016

recombination products, do not have a high IR absorption coefficient. In addition, new chemical structures involved in cross-linking may be present, but possibly only at very small concentration. Therefore, detection and detailed characterization of cross-linking using spectroscopic techniques may be difficult. A more detailed analysis is required for the identification of chemically cross-linked species.

The present paper focuses on the gel formation due to cross-linking and is part of a series of papers on the chemistry of photo-degradation of poly(neopentyl isophthalate) (PNI). In Ref. [8] full samples and the soluble part of photo-degraded PNI were studied. It was concluded that the initial step of photo-degradation of PNI is photo-cleavage according to Norrish type I. In Ref. [9] the effect of intensity and of wavelength (λ) distribution of the UV light source on the photo-degradation of PNI was investigated. Under short ($\lambda > 254$ nm) and long ($\lambda > 300$ nm) wavelength UV irradiation similar degradation products of PNI are formed. However, the presence of short wavelength radiation dramatically accelerates the overall degradation rate of PNI. This acceleration was explained quantitatively on the basis of the number of absorbed photons.

The gel formation studied in the present paper was realized by exposure of PNI, either in nitrogen or air, to UV light of a mercury lamp in a UVACUBE ($\lambda > \sim254$ nm). The gel fraction in the degraded PNI was supposed to contain the highest concentration of cross-linked structures, and is therefore the most interesting material to study the mechanism of cross-linking. The intrinsically non-soluble character of such gel severely limits the number of suitable analytical techniques that can provide structural information. Our route to obtain information on the molecular level of the cross-linking was to decompose the gel by methanolysis (break-down of the ester group) where after the decomposition products were analysed with LC-MS. When preparing this paper as based on the PhD thesis [10] of the first author we came across a contribution by Van Hoof and Deveaux [11] who applied LC-MS and other techniques to the products of glycolysis of PET that was synthesized in the presence of Ti-based catalysts. Those authors found evidence that such synthesis conditions induce the formation of biphenyl groups, as was reported earlier for other catalysts [12].

Our approach will lead to a detailed characterization of cross-linked moieties, and finally to the proposition of a mechanism of cross-linking that is supplementary to the already known phenyl-to-phenyl recombination. Of the experimental techniques employed, the methanolysis method was applied only to samples that had been photo-degraded in nitrogen, in order to avoid the additional plethora of oxidation products in the mixture of decomposition products. The other techniques were applied both to in nitrogen and to in-air degraded samples in order to demonstrate that in-nitrogen degradation tests have some relevance for photo-degradation in air as well.

2. Experimental

2.1. Materials and coating preparation

Materials and coating preparation procedures are to a large extent identical to those described in Ref [8] and will only be summarized here. The model polyester (PNI, gift from DSM) has an average molar mass of 9650 Da as determined by size exclusion chromatography and a glass transition temperature of 58 °C as determined by differential scanning calorimetry. Coatings were applied as solutions on aluminium panels resulting in a dry thickness of approximately 12 μm. The coatings were exposed at 67 °C, under either dry air or dry nitrogen conditions, to radiation in the 254–600 nm range in a UVACUBE apparatus (Dr. Hönle AG, equipped with a high pressure Mercury lamp) for 10 or 20 h. The total intensity of the light was 40 W/m^2 between 250 and 300 nm and 210 W/m^2 between 300 and 400 nm.

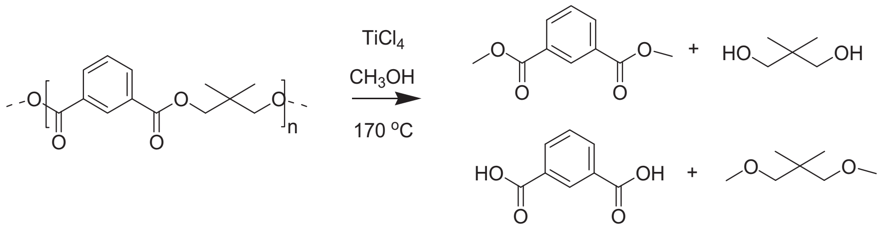
2.2. Analytical methods

Gel fractions were determined gravimetrically. The adhesion of the polyester coating to the aluminium substrate was very high and peeling off the coating for gel fraction measurement was not possible. Instead, the weight of the coating together with the substrate was measured first. Then, the polyester was washed off with THF and the weight of the bare substrate was measured. The soluble part of polyester was separated from the gel by filtration (0.2 μm PTFE filter). After evaporation of the THF (24 h at 75 °C, vacuum oven) the weight of the soluble fraction was measured. Knowing the weights of the coating with the substrate, of the bare substrate and of the soluble fraction, the weight of the gel fraction was calculated.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed using a BioRad Excalibur FTS3000MX spectrometer equipped with a diamond crystal (Golden Gate). The isolated gel was dispersed in THF and a droplet of it applied on the crystal. The THF was allowed to evaporate. Spectra of the gels were recorded in the range of 920–750 cm^{-1} with a resolution of 4 cm^{-1}.

The methanolysis reaction of the virgin polyester (blank test) and the gel were performed according to the reaction presented in Scheme 1. The reaction was carried out in a 40 ml steel reactor (Parr Instrument) containing 10 ml of methanol and 20 mg of polymer. Titanium chloride $TiCl_4$ (0.3% w/w in methanol) was used as a catalyst while the reaction conditions were 170 °C for 15 h.

High performance liquid chromatography was performed using an Agilent 1100 series system consisting of a G1311A quaternary pump, a G1322A degasser and a G1313A autosampler. An Agilent 1100, G1315B, UV-DAD (ultraviolet diode array detector) detector with detection wavelength 254 nm was used. Chromatographic separation was obtained using Zorbax RX-C8 (150 mm × 2.1 mm;



Scheme 1. Methanolysis of esters. During this reaction methanol can attack the carbonyl (−C=O) of the ester group, yielding a methyl ester (−C(O)OCH$_3$) and hydroxyl (−OH) groups. Methanol might also attack the methylene (−CH$_2$−) group, in which case carboxylic acid (−C(O)OH) and methoxy (−OCH$_3$) groups will be formed. Alternatively, OH-functional molecules can undergo Lewis-acid catalysed etherification with methanol.