Modification of $(CH)_x$ chains during thermal *cis-trans* isomerization*

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It is shown that the isomerization of *cis* polyacetylene at 195°C for long periods is accompanied by structural modifications. Infra-red and pyrolysis gas-chromatography data suggest that the aromatization process occurs even at this temperature.

Keywords Aromatization; *cis–trans* isomerization; defects; polyacetylene; pyrolysis gas chromatography; thermal degradation
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Polyacetylene $(CH)_x$ synthesized at −78°C as described by Shirakawa *et al.*[1] is almost entirely in the *cis* configuration. This isomeric form is unstable at temperatures higher than −36°C, which was determined as the threshold temperature for thermally-induced isomerization to the *trans* isomer[2]. The clearest way to achieve a particular *cis*/*trans* ratio is by thermal treatment of the pure *cis* $(CH)_x$, which has the largest chains and the smallest number of defects, between 150 and 200°C[1,3]. Usually the *cis* isomer is converted to the *trans* isomer, for characterization purposes, on heating at 200°C for 2 h[4,5].

By plotting the resistivity ρ of a *cis*-rich $(CH)_x$ sample *versus* the time t spent at a given temperature between 150° and 260°C, Rolland *et al.*[6] observed that in all cases ρ went through a minimum value ρ_{min} which decreased with increasing temperature as a consequence of the thermally-activated conductivity behaviour of $(CH)_x$. The time t_{min}, at which this resistivity minimum occurred, considerably decreased when T increased. The authors associated the resistivity increase observed for $t > t_{min}$ with a change in the intrinsic nature of the chains, i.e. gradual creation of defects along the *trans* chains. We have pointed out[7] that the appearance of defects accompanies the *cis–trans* isomerization process with a probability of defect formation which increases with temperature, e.g. two 'activated' neighbouring sequences of double bonds can isomerize or enter a Diels–Alder type cyclization reaction as depicted in *Figure 1*.

The time t_{min} for 195° and 210°C was determined as 5 min and close to 9 min, respectively[6].

In this communication we wish to report that indeed the isomerization of $(CH)_x$ at 195°C for long periods is accompanied by structure modifications.

The infra-red spectra presented in *Figure 2* shows that in the case of isomerized samples, besides the usual disappearance of the *cis* bands (446 and 740 cm^{-1}) and the augmentation of the *trans* band (1015 cm^{-1})[1], new absorptions are present at 3000–2840 cm^{-1} and 1600–1650 cm^{-1} (C–H stretching vibrations and C–C stretching vibrations from unconjugated and/or unsymmetrical conjugated systems, respectively[8]).

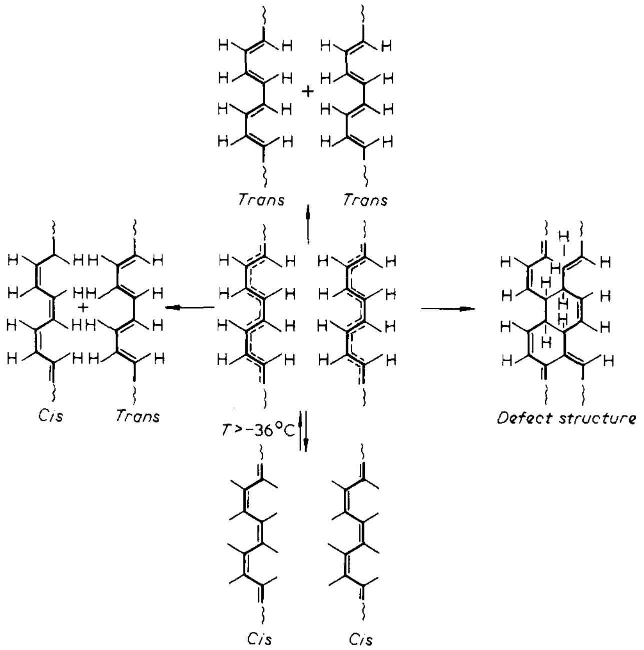

Figure 1 Schematic of defect formation during thermally activated *cis–trans* isomerization of $(CH)_x$

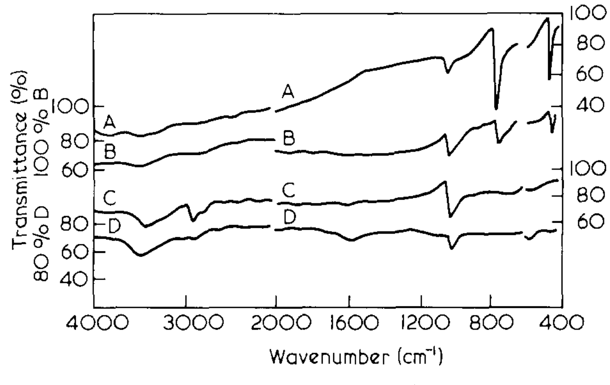

Figure 2 Infra-red spectra of different $(CH)_x$ samples: (A) parent sample, 83.5% *cis*; (B) after extraction with toluene under argon, 54.5% *cis*; (C) sample B, after standing at 195°C in vacuum for 15 h; (D) sample B, after standing at 195°C in vacuum for 30 h

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* Dedicated to Professor Otto Vogl on his 55th birthday anniversary.

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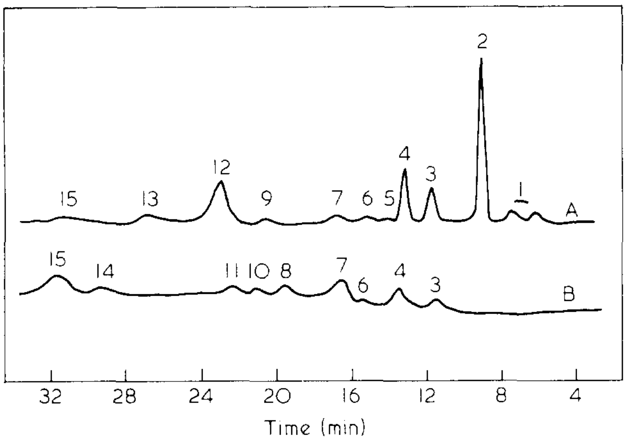

Figure 3 Gas-chromatograms of the liquid resulting after 30 h thermal treatment in vacuum at 195°C (A) and of the products released during pyrolysis of $(CH)_x$; (B) at 195°C: (1) C_5–C_6 hydrocarbons; (2) benzene; (3) toluene; (4) *m*- and *p*-xylene; (5) *o*-xylene; (6) unidentified; (7) styrene; (8) vinyl toluene; (9) indan; (10) unidentified; (11) unidentified; (12) indene; (13) divinyl benzene; (14) naphthalene; (15) methyl naphthalene

The maintainance of $(CH)_x$ at 195°C in a vacuum (7×10^{-5} torr) for long periods led to a visible degradation of the polymer, i.e. a liquid sample was collected in a cold trap (−196°C) after a prolonged degassing at 150°C. The liquid was analysed by gas chromatography and the chromatogram obtained was compared with that of the parent sample pyrolysed in the gas chromatograph at the same temperature (*Figure 3*). It can be seen that the chromatogram of the pyrolysed sample does not indicate the presence of C_5–C_6 hydrocarbons (benzene included) as decomposition products. However, benzene is the major product detected in the liquid sample collected at 195°C, suggesting that the aromatization process occurs even at this temperature.

In conclusion, the use of temperatures close to 200°C for the isomerization of *cis* $(CH)_x$, even for short periods, is not recommended, since chain defects and degradations could be induced.

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Action of far-ultraviolet radiation (185 nm) on poly(ethylene terephthalate) films: a method for controlled dry-etching

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Far-ultraviolet light (185 nm) rapidly etches poly(ethylene terephthalate) films without any subsequent processing. Both non-oxidative and oxidative mechanisms are operative.

Keywords Dry photoetching; poly(ethylene terephthalate); far-ultraviolet radiation; films; non-oxidative mechanisms; oxidative mechanisms

Introduction

In the extensive literature that exists on the action of ultraviolet light on poly(ethylene terephthalate) (PET), radiation of wavelength less than 200 nm was rarely used. This is understandable since the objective of nearly all of the investigations was the study of the degradation of the material in an adverse environment. The elegant and most exhaustive research of Wiles and coworkers[1–4] has provided a clear understanding of the reactions that take place under these conditions. We report here that far-u.v. radiation of wavelength 185 nm is highly effective in the rapid removal of PET in a controlled manner and without any subsequent treatment.

Experimental

Commercially available PET films of 250, 50 and 2.5 μ thickness were used as obtained. The sources of light were low-pressure mercury lamps of 10 W (Osram HNS 10 W/oz) or 40 W (Westinghouse G37T6VH) power. The former was enclosed in a fused-quartz well which was inserted in a water-cooled reaction chamber. The atmosphere in the chamber could be swept with air or oxygen. The 40 W lamp was used only in an air environment. The samples were placed about 0.5 cm away from the lamps. The depth and definition of the photoetching was followed by loss of weight, Taylor–Hobson Talystep measurement, and scanning electron

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