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Synthesis and characterization of a novel unsaturated polyester based on poly(trimethylene terephthalate)

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Abstract

Unsaturated aromatic polyesters were obtained by glycolysis of poly(trimethylene terephthalate) with *cis*-2-buten-1,4-diol followed by a solid-state polymerization. The glycolysis was performed in a batch mode as well as through a continuous process in a twin screw extruder. The degradation and subsequent rebuilding of the polymer chain during the course of reaction was followed by means of inherent and melt viscosity measurements, and ^{1}H NMR terminal group analysis of the intermediates and the final products. Structural investigations revealed that this new approach resulted in melt processible unsaturated polyesters with cross-linkable sites having similar characteristics to that of the virgin saturated polyester. Although the processing temperature for the different reaction steps was sufficiently high (180 − 260 °C), no thermally induced cross-linking of the incorporated unsaturated bonds could be evidenced indicating that the obtained products remained stable during the production stage. For comparison purposes, a commercial unsaturated polyester (Vestodur©) was included in the investigations. UV irradiation of thin polyester films did not result in cross-linked products but in *cis–trans* isomerization of the incorporated bisoxybutenyl unit.

Keywords: Unsaturated polyester; Glycolysis; *cis–trans* Isomerization

1. Introduction

Aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), poly(ethylene naphthalate) (PEN), and the recently introduced poly(trimethylene terephthalate) (PTT) have taken a central position under engineering plastics. As fiber, bottle, and film material or as matrix for glass-reinforced plastics, they have found a wide field of application. They are distinguished by their very good processability, low shrinkage, low water content and barrier properties. Limitations arise from relatively low glass transition temperatures resulting in reduced thermal stability. To overcome this problem polyesters are often reinforced by glass fibers and/or cross-linked by various methods. Such materials are being used in electrical applications.

Since, aromatic polyesters are relatively resistant against cross-linking by ionizing radiation, it is necessary to introduce cross-linkable groups into the polymers. This has been done in different ways. One possibility comprises the conversion of the carboxyl terminal groups of the polyesters with cross-linking agents having allyl groups and a carboxyl reactive group [1,2]. The cross-linking agent is first converted with the polyester in melt and post cross-linked by using UV irradiation.

Another versatile approach is the depolymerization of bottle PET with diols, e.g. ethylene glycol, propylene glycol [3–5], 1,2-butandiol [6–8] or dipropylene glycol [9] followed by a polycondensation with α,β-unsaturated dibasic acids or their anhydrides, e.g. maleic acid or fumaric acid. Direct conversion with an unsaturated hydroxycarboxylic acid such as *p*-hydroxycinnamic acid has also been described [10]. Unsaturated polyesters based on PET and maleic acid are often cross-linked in presence of styrene [4,6–9].

Furthermore, a number of unsaturated polyesters were synthesized by direct conversion of maleic anhydride [11] or the respective diesters [12] with various glycols. NMR spectroscopic measurements revealed that such polyesters undergo *cis–trans* isomerization resulting in a transformation of the maleate moiety into a fumarate moiety [12].

Apart from the polyesters with unsaturated dibasic acids, examples based on unsaturated dihydroxy compounds have also been described [13,14]. One of the most prominent examples is a copolyester commercialized by Degussa under

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the product line named Vestodur$^{\copyright}$. The basic structure of this copolyester is a PBT with additional *cis*-butendiol units. The synthesis comprises a typical polycondensation procedure with subsequent solid phase condensation in which in addition to 1,4-butanediol also *cis*-2-butene-1,4-diol is used [14]. Glass fiber reinforced polyesters of this type are cross-linked by ionizing radiation to give moldings with improved heat resistance, e.g. during contact with a solder bath [15,16].

This article describes an alternative process in the course of which an unsaturated polyester is obtained by glycolysis of PTT with *cis*-2-butene-1,4-diol followed by a solid phase polycondensation. The behavior of this polyester upon UV-irradiation is discussed. For comparison purposes, a sample of Vestodur$^{\copyright}$ was involved in the investigations.

2. Experimental

2.1. Materials

A sample of radiation cross-linkable PBT (Vestodur$^{\copyright}$ ZD9411; in the following referred as Vestodur$^{\copyright}$) with 20 mol% *cis*-2-buten-1,4-diol units and a melting point of about 225 °C, and an inherent viscosity (IV) of 0.645 mL/g was kindly supplied by Degussa. PTT (RTP 4700) with a melting temperature of 228 °C and an IV of 0.901 mL/g was delivered by RTP company. *cis*-2-Buten-1,4-diol, a liquid with a boiling point of 234 °C and a density of 1.07 g/cm^3, was purchased form Aldrich and used without further purification.

2.2. Glycolysis of PTT with cis-2-buten-1,4-diol in a lab scale (*1* and *2*)

In a typical example (**1c**), 19.57 g of PTT was introduced in a three-necked flask equipped with a stirrer, a nitrogen inlet and an outlet. After heating the polymer to 260 °C under nitrogen flow, 0.44 g of *cis*-2-buten-1,4-diol (5% related to the bisoxypropyl units in PTT) was added. The temperature was kept for 120 min, while a steady nitrogen flow was maintained. During this time, condensation products (e.g. propylene glycol) were removed. Then, the reaction was continued for another 60 min under reduced pressure of 500 Pa. During the whole reaction, samples were taken, the IVs of which were determined. In a second experiment, 10% *cis*-2-buten-1, 4-diol was added (**2b**). For this sample, the reaction was interrupted after 30 min without applying vacuum.

^{1}H NMR signal assignment for PTT (solvent: trifluoroacetic acid-*d* (TFA-*d*), atom positions according to Fig. 2): $\delta(^1\mathrm{H}) = 8.14$ (s, H$_1$), 4.67 (t, H$_2$), 4.61 (t, H$_7$), 4.57 (t, H$_4$), 4.04 (t, H$_9$), 3.95 (t, H$_6$), 2.42 (m, H$_3$), 2.25 (m, H$_5$), 2.20 ppm (m, H$_8$).

^{1}H NMR signal assignment for **1c** and **2b** (solvent: TFA-*d*, atom positions according to Fig. 2): same signals as PTT and additional signals at 6.03 (t, H$_{11}$), and 5.15 (d, H$_{10}$) ppm.

Regarding the signal positions, the spectra of **1c** and **2b** do not differ from each other.

A sample overview is given in Table 1.

2.3. Glycolysis of PTT in a twin screw-extruder (*3*)

Glycolysis of larger amounts of PTT through a continuous process was carried out in a Werner and Pfleiderer co-rotating twin-screw extruder ZSK30 ($L/D = 41$) equipped with a general screw type for polyester melt mixing. The processing temperature was 230 °C. PTT granules were fed into the extruder hopper with a feeding rate of 3 kg/h at a screw rotation speed of 30 rpm. Liquid *cis*-2-buten-1,4-diol (47.5 g/kg PTT) was added by a gravimetric feeding system equipped with a feed pump through a pipe to the extruder barrel near the feeding zone. An appropriate ventilation system was used for degassing near the extruder die. A drastic drop in the viscosity of the extrudate was observed so that no strand could be

Table 1
Sample overview

Sample	[BD]^a (feed) (mol%)	Reaction conditions^b	IV (mL/g)	[BD]^c (NMR) (mol%)
PTT	–	Virgin	0.901	–
1a^d	–	Lab/260 °C/N$_2$, 0 min	0.863	–
1b	5	Lab/260 °C/N$_2$, 30 min	0.390	3.0
1c	5	Lab/260 °C/N$_2$, 120 min/vac., 60 min	0.887	2.5
2a^d	–	Lab/260 °C/N$_2$, 0 min	0.783	–
2b	10	Lab/260 °C/N$_2$, 30 min	0.199	7.0
3a^d	–	Extr/230 °C/air, <5 min	0.833	–
3b	10	Extr/230 °C/air, <5 min	0.190	8.2
3c	10	SSP/180 °C/vac., 48 h	0.453	6.0
3d	10	SSP/190 °C/vac., 24 h	0.610	5.4
3e	10	SSP/200 °C/vac., 24 h	0.758	6.3
Vestodur$^{\copyright}$	20^e	Virgin	0.645	17.0
Vestodur$^{\copyright}$-SSP1	20^e	SSP/190 °C/vac., 20 h	0.942	16.7
Vestodur$^{\copyright}$-SSP2	20^e	SSP/190 °C/vac., 24 h	1.105	16.0

[a] Content of *cis*-2-buten-1,4-diol in the feed related to bisoxypropyl units in PTT.

[b] Conditions for glycolysis in a lab scale (Lab), in a extruder (Extr) and for solid-state polymerization (SSP).

[c] Content of incorporated bisoxybutenyl units determined by ^{1}H NMR from the signal intensities of olefinic protons of BD units and internal methylene groups of propylene (PTT) or butylenes diol (Vestodur$^{\copyright}$) units (estimated error ±0.5 mol%).

[d] Reference sample of molten PTT before BD was added.

[e] Content of bisoxybutenyl units as given by the supplier.

formed. The extrudate was quenched in a water bath and a very brittle product was obtained. After shredding into small pieces, the product was dried for 4 h in a vacuum oven at 80 °C (sample **3b**). Then, solid-state polymerization (SSP) was performed to increase its molecular weight (samples **3c–e**, see Table 1).

^1H NMR signal assignment of **3b** (solvent: TFA-*d*, atom positions according to Fig. 2): same signals as PTT and additional signals at 6.03 (t, H_{11}), 5.97 and 5.93 (2m, –CH=CH– of BD_{term}), 5.85 (t, –CH= of BD), 5.15 (d, H_{10}), 5.04 (d, $CH_2O(O)C$ of BD_{term}), 4.52 (d, CH_2OH of BD_{term}), 4.42 (d, CH_2 of BD) ppm.

After SSP, the same ^1H NMR signals as in samples **1** and **2** were found.

2.4. Solid-state polymerization

To enhance the molecular weight, glycolyzed PTT and Vestodur© were subjected to SSP at 180, 190 and 200 °C, respectively. For smaller amounts (up to 10 g), SSP was performed in a flask under nitrogen flow or under vacuum. For larger amounts a nitrogen flushed vacuum oven was used. Different temperatures and times were applied to obtain a product with a molecular weight similar to that of the virgin PTT (Table 1).

2.5. Inherent viscosities

Inherent viscosities (IV) were determined in a 60/40 mixture of phenol/tetrachloroethane. One hundred milligram of the sample was dissolved in 20 mL of the mixed solvent during 8 h at 60 °C and then passed through a filter. The intrinsic viscosity of the clear solution was measured at 25 °C using an Ubbelohde capillary viscometer (capillary no. Ia).

2.6. Sample preparation

Films (ca. 0.1 mm) were obtained by pressing the polymers at 230–240 °C on a hot press between two aluminum foils. To adjust the film thickness, a 0.1 mm thick frame was used as distance piece. Transparent amorphous films were obtained by rapid cooling in cold water whereas slow cooling on air resulted in opaque crystalline films.

2.7. UV irradiation

UV irradiation was performed with a 200 W HgXe arc lamp (Oriel Instruments, Stratford, CT/USA). The sample was placed on an optical bench directly in front or in a distance of 10 cm from the lamp. The irradiation time was 2 h.

2.8. NMR measurements

^1H NMR measurements were carried out on a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^1H. The samples were dissolved in trifluoroacetic acid-d_1 and measured immediately to avoid reactions of hydroxy end groups with the solvent. The spectra were referenced on internal sodium 3-(trimethylsilyl)-3,3,2,2-tetradeuteropropionate ($\delta(^1H)=0$ ppm).

2.9. Rheological measurements

The rheological measurements were performed using an ARES oscillatory rheometer (Rheometric Scientific, USA) with a parallel plate (plate diameter of 25 mm, gap of 1.5 mm) at 230 and 250 °C under nitrogen atmosphere. Angular frequency sweeps were applied within 0.1 and 100 rad/s. For each sample, prior to the frequency sweeps, a strain sweep (1–100%) was also performed. The strains used for all the measurements were within the linear range of the viscoelastic response. The variation of the complex viscosities (η^*) versus applied frequency was used for comparing the samples.

3. Results and discussion

The conversion of PTT with 5 mol% (sample **1**) and 10 mol% (sample **2**) *cis*-2-butene-1,4-diol (BD) related to the propane-1,3-diol units in the polyester was performed at 260 °C in a glass flask under stirring. A steady nitrogen flow was applied in order to remove the major part of propane-1,3-diol formed during the reaction and to protect the reaction mixture from thermo-oxidative processes. The course of reaction is demonstrated in Fig. 1 by means of the IV values of the samples taken during the reaction. Immediately after adding the BD, a strong decrease in IV is observed which is more pronounced in the case of 10% BD added. During the reaction with the diol, the ester bonds are cleaved resulting in a hydroxy terminated PTT oligomer (Scheme 1). Extension of the reaction time causes a rebuilding of the polymer chain. In the case of the reaction mixture with 5 mol% BD, the IV of the starting PTT is reached after approximately 3 h (sample **1c**). It has to be mentioned that during the last 60 min vacuum was applied in order to remove residual diol necessary to achieve a high molecular polyester.

The course of reaction was also followed by ^1H NMR spectroscopy. A section of the spectra of sample **1b** and the sample **1c** obtained after 60 and 180 min, respectively,

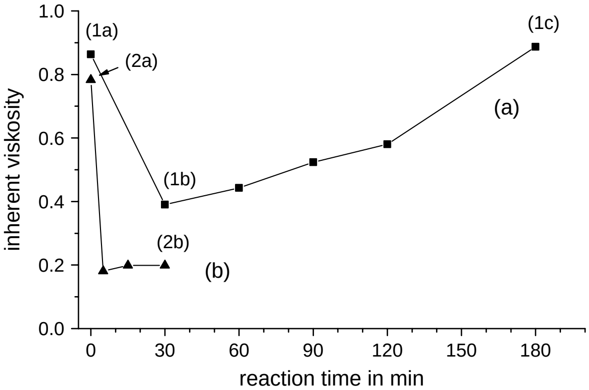
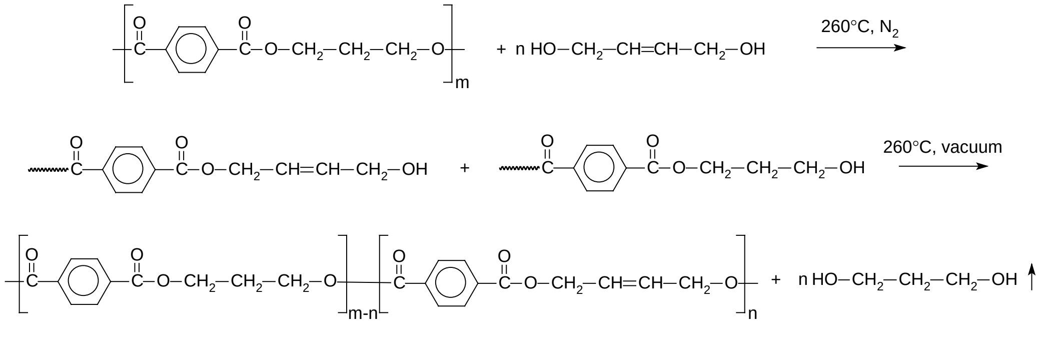


Fig. 1. Conversion/time curves of the reaction of PTT with (a) 5 mol% (**1**) and (b) 10 mol% (**2**) *cis*-2-buten-1,4-diol.



Scheme 1.

and of PTT is shown in Fig. 2. Apart from the expected signals, three signals belonging to a dipropylene glycol unit are found in the spectrum of PTT (2.25, 3.95, 4.57 ppm). The signal at 4.04 ppm could be assigned to the hydroxy propylene terminal group. After conversion with BD, initially the intensity of the latter increased distinctly (**1b**) and diminished after continuation of the reaction (**1c**). Two new signals at 5.15 and 6.04 ppm belong to the incorporated BD moiety, the intensity of which does not change significantly during the whole reaction time. Signals of BD terminal groups could not be found in the spectra. This shows that BD is completely incorporated into the PTT chain after 30 min. From the signal intensity at 5.15 and 6.04 ppm related to the signals of the propylene diol moiety of PTT, a BD content of 2.5% could be approximated for the final product **1c**. That means that only 50% of BD was incorporated into PTT during the reaction. The remaining 50% escaped from the reaction mixture in a very early stage (<30 min) of conversion via the nitrogen stream applied. The BD content of sample **2b** was approximately 7% showing that in this case 70% of BD added was incorporated into PTT. The complete ^{1}H NMR signal assignment of PTT and its modified form is given in Section 2.

Larger amounts of glycolyzed PPT were obtained by conversion in a twin screw extruder (sample **3**). Compared to the reaction in the lab-scale the reaction temperature was reduced to 230 °C. The reason for this was the very low viscosity of the reaction product. Lowering the processing temperature improved handling of the extruded melt and should prevented thermo-oxidative decomposition caused by traces of oxygen. The latter was assumed to be negligible because of the low residence time of the melt in the extruder.

During extrusion, 10% BD related to the propylene diol moieties in PTT were fed continuously. Extrusion of PPT without BD (**3a**) resulted in a slight decrease in the IV from 0.863 to 0.833 dL/g, whereas in presence of BD, a very distinct decrease to 0.190 dL/g was observed (**3b**). ^{1}H NMR spectra of extruded samples comprise all features found for the samples synthesized in a laboratory scale as shown in Fig. 2. However,

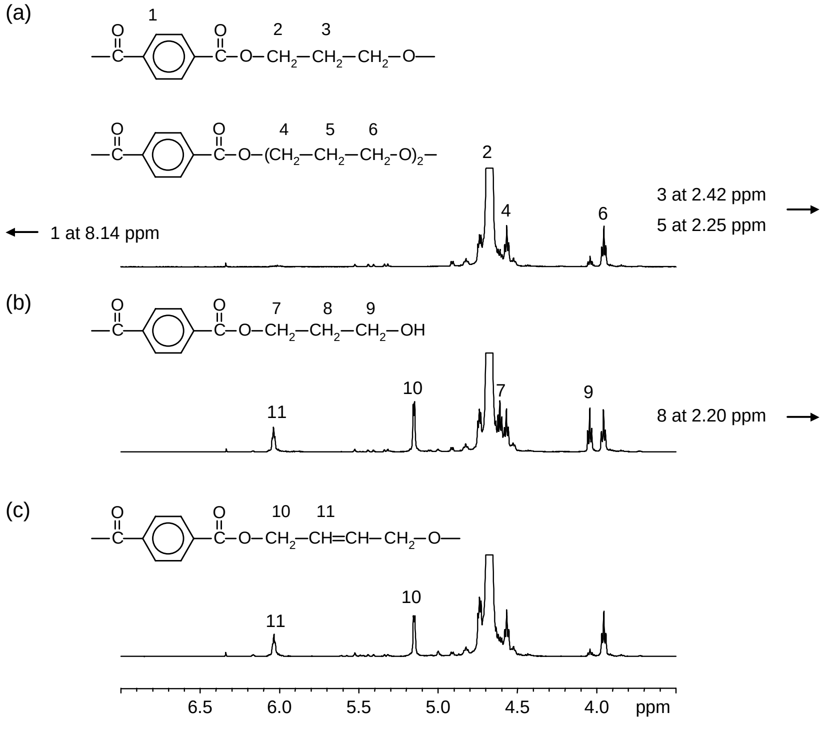


Fig. 2. ^{1}H NMR spectra (section) of (a) PTT, (b) **1b**, and (c) **1c**.

additional ^{1}H NMR signals in reasonable intensity prove the presence of both unconverted BD and BD terminal groups (BD$_{\mathrm{term}}$) (Section 2). Obviously, the incorporation of BD during the extrusion process was incomplete owing to the short residence time (<5 min) in the extruder.

The extruder product **3b** was subjected to a solid-state polymerization (SSP) at 180, 190, and 200 °C. The increase in IV over the annealing time is demonstrated in Fig. 3. At 180 °C a steady increase in IV from 0.190 to 0.453 dL/g is observed within 48 h (**3c**). At 190 °C, the annealing effect is much more pronounced. A product with an IV of 0.610 dL/g is obtained after 24 h (**3d**). Further annealing did not result in higher IV values. The highest IV obtained (0.758 dL/g) possessed a sample which was annealed for 24 h at 200 °C (**3e**). This value is close to the value of the starting PPT and comparable with that of Vestodur© (0.645 dL/g). The IV of the latter could also be increased to 1.105 dL/g after annealing for 24 h at 190 °C (Vestodur©-SSP2).

The additional signals in the ^{1}H NMR spectrum found in the extruder product **3b** disappeared completely after SSP. The spectra of all samples obtained after annealing at different temperatures (**3c**–**e**) match satisfactory to that of **1c** shown in Fig. 2. Differences between the annealed samples are only seen in the intensity of the terminal group signal at 4.04 ppm owing to the different molecular weights achieved. The content of incorporated BD varied only slightly from sample to sample between 5.4 and 6.3%. These contents are significantly lower than that of the sample before SSP (8.2%). Obviously, SSP results in an incorporation of BD into the polymer chain and allows removing unconverted BD completely. Relatively homogeneous samples with increased molecular weight were obtained. The incorporation of BD was not complete (ca. 60%) but can be improved by increasing the residence time of the extruder. The ^{1}H NMR spectrum of the final product did not reveal distinct signals of structures related to side reactions such as oxidation of C=C bonds or cross-linking. Obviously, this reactions play a secondary role under the reaction conditions chosen although they cannot be excluded completely.

The increased molecular weights of the modified samples after SSP also influence the rheological behavior. The variations of the melt viscosities of PTT, **3b**, **3d**, and **3e** with the shear rate are shown in Fig. 4. Similarly, as demonstrated by means of the IV values, a strong drop in the melt viscosity is achieved after conversion of PTT with BD (**3b**), which after SSP raises again up to the level of unmodified PTT. In each case, the melt viscosity is almost independent of the shear rate indicating that thermally induced cross-linking is unlikely. Contrary to this, the melt viscosity of Vestodur© in its virgin state shows a shear thinning behavior over the whole frequency range (Fig. 5). This points to a slightly cross-linked product. This effect becomes even more pronounced after SSP. Obviously, the higher content of unsaturated BD in Vestodur© makes this polymer more susceptible to thermal cross-linking.

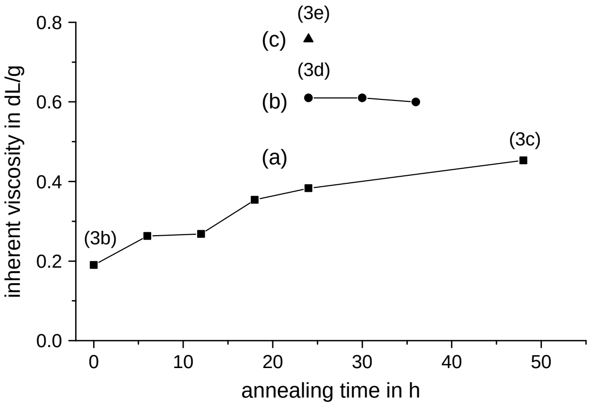


Fig. 3. Increase of the inherent viscosity of **3b** during solid-state polymerization at (a) 180 °C, (b) 190 °C, and (c) 200 °C.

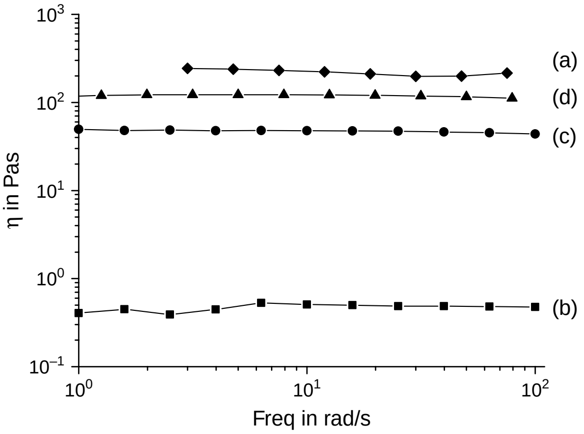


Fig. 4. Variations of melt viscosities of (a) PTT, (b) **3b**, (c) **3d**, and (d) **3e** at 230 °C with the shear rate.

Some of the unsaturated polyesters including Vestodur© were irradiated by UV light to figure out whether radiation induced cross-linking is possible. Since, the depth of penetration is limited for UV light, irradiation was performed on ca. 0.1 mm thick films. The results have to be regarded provisional since the irradiation equipment used did not allow to adjust defined conditions. Thus, it was not completely possible to avoid heating of the sample by the UV lamp. Yet, the result allow to draw some interesting conclusions.

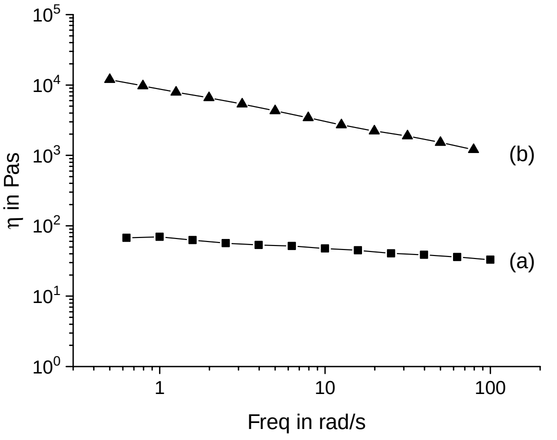


Fig. 5. Variations of melt viscosities of Vestodur© at 250 °C with the shear rate (a) virgin sample, (b) after 20 h solid-state polymerization at 190 °C (Vestodur©-SSP1).

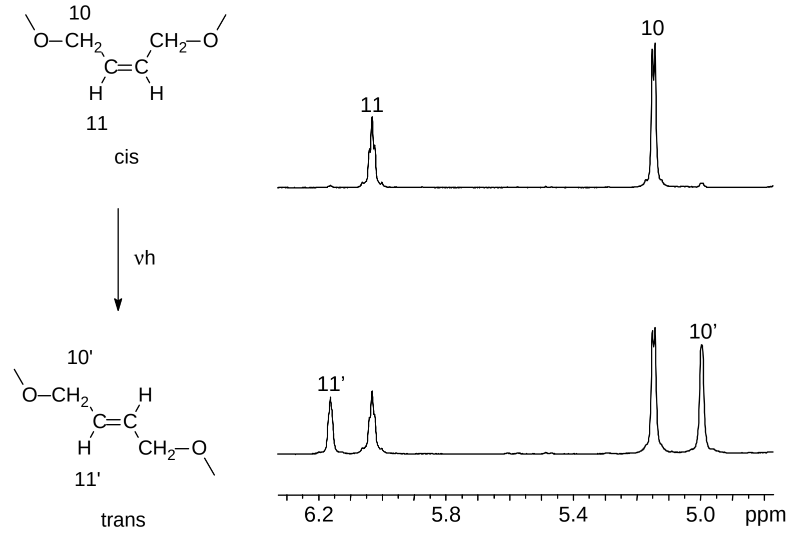


Fig. 6. ^{1}H NMR spectra (section) of Vestodur© (a) virgin sample and (b) after UV irradiation for 2 h.

Provided sample heating was reduced to a minimum, no change in IV was observed after irradiation. This implies that UV induced cross-linking of solid films failed. Obviously, the mobility of the polymer chain is too low to induce cross-linking. However, some remarkable alterations in the ^{1}H NMR spectra of all irradiated samples could be evidenced. As an example, a section of the spectrum of irradiated Vestodur© is shown in Fig. 6. Beside the two signals of the *cis*-bisoxybutenyl moiety in the polymer at 5.15 and 6.04 ppm, two additional signals at 4.99 and 6.17 ppm appear which can be assigned to the *trans*-bisoxybutenyl moiety. This means that during UV irradiation *cis–trans* isomerization occurs, whereas cross-linking is negligible. The modified PTT samples **1**, **2**, and **3** showed the same behavior.

In some irradiation attempts where the sample was placed near the UV lamp, insoluble products were obtained which is an indication for cross-linking reactions. This was mainly observed in case of Vestodur© possessing a higher content of unsaturated bonds than the modified PTTs **1**, **2** and **3**. However, the insufficient experimental set up does not allow to conclude whether cross-linking is caused by a higher dose of radiation or by increased chain mobility due to heating of the sample by the UV lamp. This demands further investigations.

4. Conclusions

Glycolysis of PTT with *cis*-2-buten-1,4-diol (BD) and subsequent solid-state polymerization has proven to be an alternative for the preparation of unsaturated polyesters. Glycolysis performed successfully in a batch mode and also continuously in an extruder resulted in the formation of oligomers with strongly decreased inherent and melt viscosities. In order to rebuild the molecular weight, a condensation process was followed which was carried out either in melt or in the solid-state. In both cases satisfactory results were obtained. Although the temperatures of glycolysis and post-polycondensation were sufficiently high, the incorporated bisoxybutenyl unit in the polymer has proven to be stabile against thermally induced cross-linking and the final products remained completely soluble. However, cross-linking cannot be excluded completely under certain conditions. In the case of the commercial polymer Vestodur©, shear thinning over the whole frequency range was observed indicating that slight cross-linking might have occurred which after SSP became more significant. This can be explained by the higher amount of double bonds in this polymer which was more than twice as high as in the polymers obtained according to the procedure described here.

Furthermore, NMR spectroscopy on intermediates and final products of the modified PTT revealed that BD is incorporated with both sides into the polymer chain almost completely and relatively fast. Only in a very early state of the reaction as for example for the product obtained after glycolysis in an extruder, BD terminal group could be evidenced. After slightly increased reaction times or SSP, BD terminal groups disappeared. Instead, the signal of trimethylene terminal groups increased and diminished after further reaction.

It is well known that unsaturated polyesters can be cross-linked by ionizing radiation. For polyesters containing bisoxybutenyl units as for example Vestodure©, cross-linking has mainly been described in the patent literature. According to our knowledge, UV irradiation of bisoxybutenyl unit containing polyesters has not been the subject of a publication so far. Our investigations revealed that UV irradiation of thin films of such polyesters resulted in a *cis–trans* isomerization of the bisoxybutenyl unit. This effect might be interesting for radiation induced alterations of the morphology of polymers. Cross-linking reactions could be excluded, as long the temperature of the sample did not increase during irradiation. Additional results suggest that UV cross-linking might be possible at higher temperature. To verify this, further investigations are required.

Eventually, we can state that the new approach to prepare unsaturated polyesters as described here based on a glycolysis of PTT in an extruder followed by a SSP is very versatile and can certainly be applied to other polyesters as PET, PBT and PEN or even to aliphatic polyesters.

Acknowledgements

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