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Aromatic poly(ester–urethanes): effect of the polyol molecular weight on the photochemical behaviour

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Abstract

Photooxidation of 4,4′-methylene bis(4-phenylisocyanate) and toluene diisocyanate based poly(ester–urethanes) has been followed by means of Fourier transform infrared spectroscopy as a function of soft segment molecular weight. The results have been related to the hard/soft segment phase mixing, studied by differential scanning colorimetry.

The extent of the photolysis reaction in the urethane linkage is more relevant in higher soft segment molecular weight based polymers. The phase separated structure is a critical factor which must be taken into account in order to study the extent of the photodegradation of the hard segments in aromatic poly(ester–urethanes). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Aromatic polyester urethanes; Photodegradation

1. Introduction

Segmented polyurethanes are block copolymers which consist of polyol sequences (soft segments) and urethane sequences (hard segments) [1]. The segmented urethane building blocks (hard and soft segments) are thermodynamically incompatible but due to their chemical linkage the phase separation is not complete and, therefore, this kind of polymers present a segregation in microdomains [2].

The unusual properties displayed by segmented polyurethanes are directly related to their two-phase microstructure. Polyurethanes are widely used as surface coatings in outdoors applications, where the photo-oxidative behaviour is a decisive factor which can lead to the failure of an excellent mechanical properties formulation.

Aromatic diisocyanate based polyurethanes turn yellow on storage or in actual use, so they are often replaced by the more expensive aliphatic diisocyanate based polyurethanes which show markedly better resistance to yellowing.

Most of the studies on the photodegradation of polyurethanes [3] are centred around the commercially available polyurethanes derived from aromatic diisocyanates such as toluene diisocyanate (TDI) and 4,4′-methylenebis(4-phenylisocyanate) (MDI). Aliphatic diisocyanate based polyurethanes show remarkable photoresistance so that their photodegradation studies are limited [4,5].

Taking into account the effect of excitation wavelengths, Gardette and Lemaire [6] have proposed a photodegradation mechanism for aromatic diisocyanate based polyurethanes that is currently accepted. According to these authors, the photodegradation of the urethane linkage in aromatic diisocyanate based polyurethanes proceeds by two mechanisms. At short wavelengths (<340 nm), the photolysis proceeds through a photo-Fries type reaction. In presence of oxygen, oxidation of urethane hard segments occurs in MDI based polyurethanes. This reaction involves a radical attack on the central methylene carbon of the aromatic structures with the subsequent formation of hydroperoxides, leading to the formation of quinone–diimide structures as well as benzoic acid end groups.

In addition, the physical state [7] of the polymer is an important factor which controls the magnitude of the photodegradation. However, very few studies have referred to the effect of the content and molecular weight of the soft segments on the photodegradation behaviour, so that the influence of the physical state on the photodegradation is not fully understood. In this sense, Frish et al. [8], in their research on aromatic polyurethanes, have concluded that the resistance to photodegradation is enhanced with both the increase of hard segment concentration and the decrease of soft segment molecular weight. Hoyle et al. [9], working with the same type of systems, have proposed that the extent of the photolytic decomposition is inversely dependent on the degree of hydrogen bonding in the aryl carbamate groups present in the polyurethane backbone.

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Table 1
Nomenclature describing the obtained polymers (TDI, toluene diisocyanate; MDI: 4,4′-methylene bis(4-phenyisocyanate); BD: 1,4-butanediol; PECAP1250, poly(ε-caprolactone) with $M_w = 1250$; PECAP2000, poly(ε-caprolactone) with $M_w = 2000$; PTMO2000, poly(tetramethylene oxide) with $M_w = 2000$; % hard segment (weight of diisocyanate + weight of BD)/(total weight))

Isocyanate	Chain extender	Soft segment	% Hard segment	Nomenclature
TDI	BD	–	100	TDIBD
MDI	BD	–	100	MDIBD
TDI	BD	PECAP1250	31	TC1.31
TDI	BD	PECAP2000	22	TC2.22
MDI	BD	PECAP1250	38	MC1.38
MDI	BD	PECAP2000	28	MC2.28
TDI	BD	PTMO2000	22	TT2.22
MDI	BD	PTMO2000	28	MT2.28

In a recent series of papers [10,11] devoted to the photodegradation of segmented aromatic poly(ether–urethanes), a mutual stabilisation effect between the hard and the soft segments has been found. This effect of stabilisation has been related to the physical state of the polymer, being more prevalent in polyurethanes with a higher phase mixing between hard and soft segments. Photo-oxidative studies [11] of aliphatic diisocyanate-based poly(ester–urethanes) and poly(ether–urethanes) have shown that ether soft segments induce the oxidation of aliphatic hard segments. Ester soft segments, however, show a markedly higher photoresistance and do not induce the photooxidation of aliphatic urethane hard segments.

In the present paper, photodegradation studies by means of Fourier transform infrared (FTIR) spectroscopy of aromatic diisocyanate based poly(ester-urethanes) are presented. The aim of this work is to elucidate the role of ester soft segments in hard segment photodegradation. The results are compared with those obtained in a previous work for aromatic poly(ether–urethanes).

2. Experimental

4,4′-Methylene bis(4-phenylisocyanate) (MDI) (Aldrich) and 2,4-toluene diisocyanate (TDI) (Aldrich) mixture of isomers 2,4 and 2,6 were distilled under reduced pressure. *N*,*N*′-dimethyl formamide and 1,4-butanediol (Aldrich) were distilled under vacuum and then stored over activated 4 Å type molecular sieves. Poly(ε-caprolactone) (Aldrich) ($M_w = 1250$ and 2000) was degassed under vacuum at 50°C overnight. The average molecular weight was calculated using ^{1}H NMR. Stannous Octoate (Sigma) was used as received.

Linear polyurethanes obtained from 1,4-butanediol and MDI or TDI were synthesised by solution polymerisation without catalysis [12]. Segmented polyurethanes were synthesised in solution by a catalysed prepolymer technique [13]. A description of the obtained polymers is given in Table 1.

The polymer samples were irradiated in an accelerated weathering device equipped with a xenon arc light source. The more energetic radiation (not presented in natural weathering) was eliminated using a 300 nm borosilicate filter. The temperature inside the irradiation chamber was kept constant using a ventilator. The average temperature measured in a black panel thermometer was 45°C over the sample.

The segmented samples to be irradiated were prepared by casting in anhydrous dimethyl formamide over potassium bromide windows. The samples were dried under vacuum, initially at room temperature and afterwards at 60°C. Sample thickness was controlled by the regulation of the absorbance of the carbonyl stretching vibration to 1.0.

In order to obtain reproducible results, only one sample was used for each formulation. The samples were taken out from the weathering device at different exposition times and the FTIR spectra were recorded.

FTIR spectra were recorded using a Nicolet 5DXC spectrometer equipped with a DTGS detector. The spectra

Table 2
Thermal transitions for the studied polymers

Polymer	% Hard segment	Soft segment molecular weight	Thermal transitions (°C)
PECAP1250	0	1250	T_g(onset) = −70 T_m(max) = 48
PECAP2000	0	2000	T_g(onset) = −67 T_m(max) = 53
MDIBD	100	–	T_g(onset) = 99 T_m(max) = 222
TDIBD	100	–	T_g(onset) = 99
MC1.38	38	1250	T_g(onset) = −39
MC2.28	28	2000	T_g(onset) = −42 T_m(max) = 44
TC1.31	31	1250	T_g(onset) = −28 T_m(max) = 55
TC2.22	22	2000	T_g(onset) = −69 T_m(max) = 42

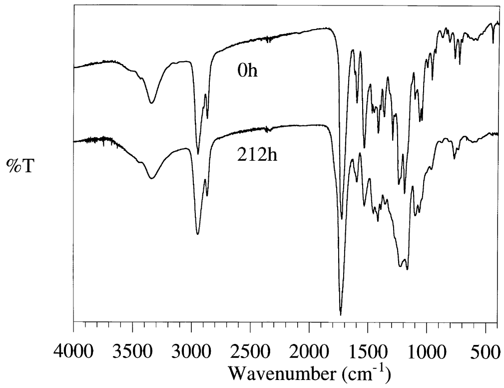

Fig. 1. FTIR spectra of TC1.31 before and after irradiation.

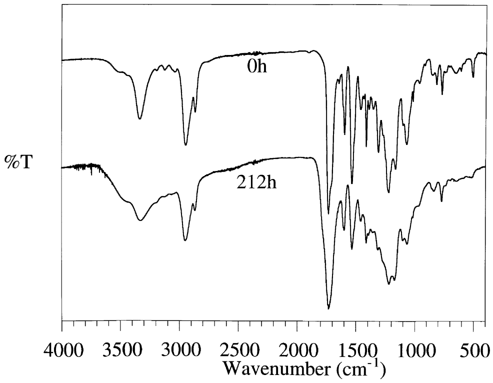

Fig. 3. FTIR spectra of MC1.38 before and after irradiation.

were obtained at a resolution of 2 cm^{-1} using 64 scans summation.

Differential scanning calorimetric (DSC) studies were carried out with a Perkin–Elmer DSC-2. The heating rate used was 20°C min^{-1} over a temperature range from −120 to 240°C in a nitrogen atmosphere. The sample weight was approximately 10 mg. Dodecane and indium were chosen as calibration standards.

3. Results and discussion

3.1. Compatibility between hard and soft segments: DSC studies

It is well established that segmented polyurethanes present a phase separated structure as a consequence of the thermodynamic incompatibility between soft and hard segments. Soft segment glass transition temperature (T_{gs}) has usually been used to determinate the compatibility between phases, where a T_{gs} close to the one obtained for pure soft segment (poly(ε-caprolactone)) reflects a very low phase mixing.

Table 2 summarises DSC results for the studied systems. As can be seen, regardless of molecular weight, poly(ε-caprolactone) depicts a glass transition temperature about −70°C and a melting point close to 50°C. Non-segmented polyurethanes based on MDI and TDI (4,4′-methylene bis(4-phenylisocyanate)–1,4-butanediol (MDIBD) and 2,4-toluene diisocyanate–1,4-butanediol (TDIBD)) show the same T_g value. MDIBD also shows an endothermic peak at 222°C. Only amorphous structures are obtained in TDIBD because of the asymmetric structure of the main isomer (2,4-TDI).

In the case of segmented poly(ester–urethanes), those samples obtained from 1250 molecular weight soft segment show an increase in T_{gs} when compared with the obtained from pure soft segment, indicating some extent of soft/hard segment phase mixing. This increase can be explained on the basis of a decreased mobility of the soft segments because of their attachment to stiffer urethane groups and/or the penetration of isolated hard segment units into the soft segment phase.

However, the systems based on 2000 molecular weight poly(ε-caprolactone) show a different calorimetric behaviour in the sense that a T_{gs} nearly the same as those obtained for pure poly(ε-caprolactone) is obtained, suggesting a higher phase separation as soft segment molecular weight increases. In addition, TC2.22 shows a T_{gs} lower than the corresponding to MC2.28, indicating that TDI based polyurethanes show a lower phase interaction than MDI based systems. This behaviour has already been

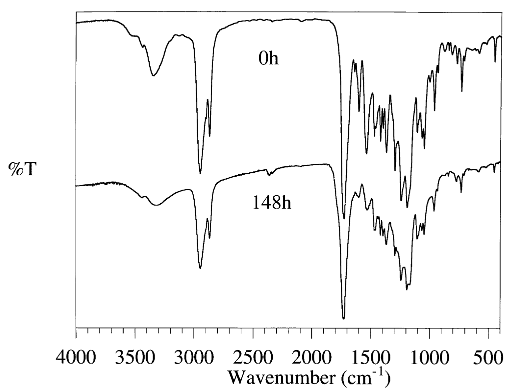

Fig. 2. FTIR spectra of TC2.22 before and after irradiation.

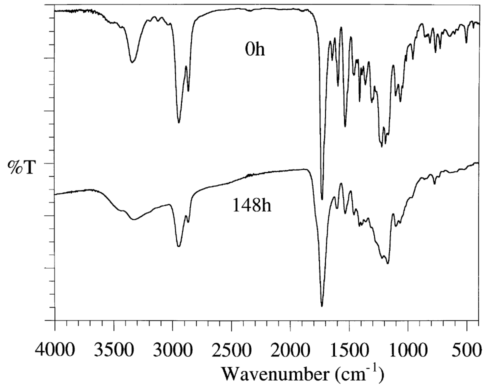

Fig. 4. FTIR spectra of MC2.28 before and after irradiation.

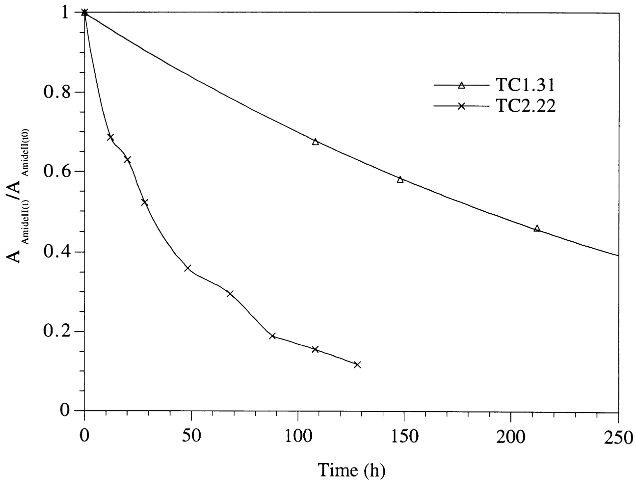

Fig. 5. Normalised decrease of amide II band for TDI based polyurethanes as a function of the irradiation time.

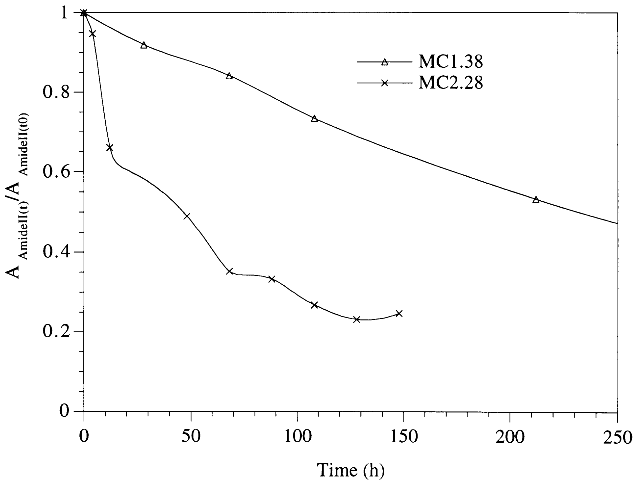

Fig. 6. Normalised decrease of amide II band for MDI based polyurethanes as a function of the irradiation time.

reported on aromatic poly(ether–urethanes) [10] and can be explained with a viscosity/mobility argument, as proposed by Li et al. [14].

Similar results have also been obtained by means of small angle X-ray scattering (SAXS) [15], dynamic mechanical thermal analysis (DMTA) [16] and DSC [17–20].

3.2. Photodegradation of TDI and MDI based poly(ester-urethanes)

Changes in the IR spectra of MDIBD and TDIBD, as a result of the exposition to UV radiation, were studied in a previous work [10]. The IR spectra of segmented polyurethanes TC1.31, TC2.22, MC1.38 and MC2.28, before and after irradiation, are shown in Figs. 1–4. Table 3 describes the IR characteristic absorption frequencies of aromatic poly(ester–urethanes) [21].

The modifications of the IR spectra can usually be separated into those concerning the soft segment and those of the urethane functions. In these spectra, however, no decrease of the IR bands assigned to the ester function is observed, in accordance with previously reported data for polyadipate [5] based polyurethanes. The main spectral changes correspond exclusively to urethane groups, and, therefore, the evolution of the spectra of irradiated poly(ester–urethanes) may be interpreted from those of TDIBD and MDIBD. For these systems, the predominant change observed was a decrease of the urethane characteristic IR absorption bands at 1720 cm^{-1} (carbonyl group stretching vibration) and 1533 cm^{-1}, which is a combined vibration of the C–N stretching vibration and N–H bending vibration, named amide II band. In addition, a broadening of the N–H stretching vibration band was also observed, which suggests the formation of hydroperoxy groups.

The extent of the photodegradation of the urethane groups for segmented polyurethanes has been studied by means of the decrease of the amide II band. The obtained results are displayed in Figs. 5 and 6. Both figures reflect that for TDI and MDI based poly(ester-urethanes), the higher the soft segment molecular weight the lower is the photoresistance of the sample. These results can be explained upon the basis of a stabilisation effect between soft and hard segments, and the extent of this stabilisation will be more prevalent for samples with higher phase mixing.

These considerations are in accordance with the DSC measurements where a very low hard/soft segment interaction has been observed for those systems with a higher molecular weight soft segment (TC2.22 and MC2.28). The stabilisation effect has already been mentioned by other authors [22] about thermal degradation of the urethane linkages.

Table 3
Infrared absorption frequencies in polyester urethanes (w, weak; vw, very weak; m, medium; s, strong; vs, very strong; sh, shoulder, υ = stretching; δ = bending; w, wagging; δoop = out of plane bending)

Frequency (cm^{-1})	Relative intensity	Main assignments
3420	vw, sh	υ((N–H) free
3320	vs	υ((N–H) associated
1750–1710	vs	υ((C=O) in ester υ C=O in urethane)
1600	m	υ(C=C) in aromatic ring
1533	S	υ(C–N) + δ (N–H) (amide II)
1475	w	δ(CH_2
1263	s	υ(C–N) + δ (N–H) (amide III)
1250	s	υ(C–O–C) in ester
1180	s	υ(C–O–C) in ester
816	w	δoop = C–H in MDI and TDI
773	w	δoop in COO urethane
638	w	w (N–H) amide V
612	vw	Aromatic in plane deformation vibration in p-rings
513	vw	Aromatic oop deformation vibration in p-rings
455	vw	Aromatic oop deformation vibration in 1,2,4 rings

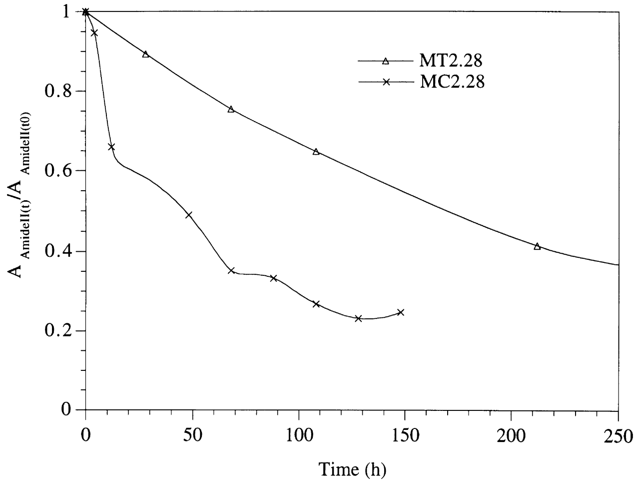

Fig. 7. Normalised decrease of amide II band for MT2.28 and MC2.28 as a function of the irradiation time.

If we compare these results with those obtained for aromatic poly(ether-urethanes) [10], we must point out that those systems exhibited a mutual stabilisation effect between the soft and the hard segments which was strongly dependent on the interaction between both types of segments. The extent of this interaction was related to the molecular weight of the soft segment.

Figs. 7 and 8 show the evolution of the normalised area of the amide II band for the MDI and TDI based polyesters and polyethers with the irradiation time. As can be seen in Fig. 7, in MDI based polymers, the extent of the urethane linkage photodegradation is higher in the ester soft segment based polymer sample than in the one based on ether soft segment.

Fig. 8 shows the same comparison for the TDI based samples. The urethane linkage in ester based polymers is once again more unstable than in poly(ether–urethanes).

It can be established that the difference in behaviour between ether and ester based polyurethanes is due to a distinct extent of the hard/soft segment interactions, which in turn depend on the hydrogen bonding association between the different groups.

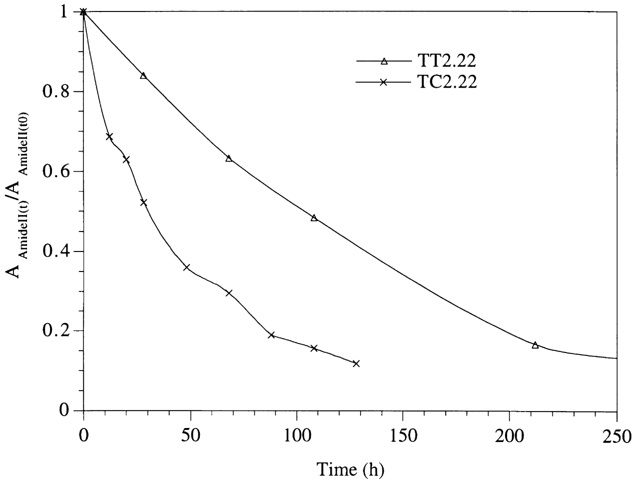

Fig. 8. Normalised decrease of amide II band for TC2.22 and TT2.22 as a function of the irradiation time.

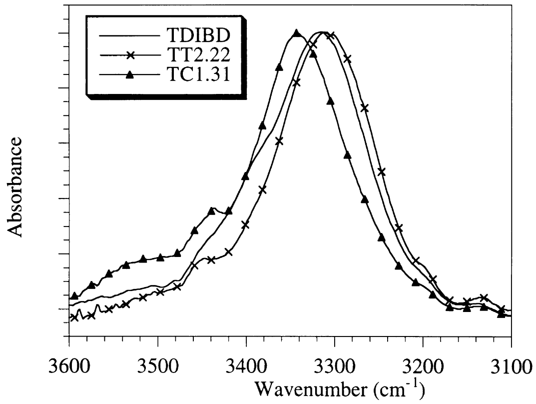

Fig. 9. FTIR N–H stretching region for TDIBD, TC1.31 and TT2.22.

In polyurethanes, hydrogen bonding association in the hard segments takes place between urethane carbonyl and N–H groups. In segmented polyurethanes, the ether oxygen of the polyether block or the ester carbonyl of the polyester block competes with the urethane carbonyl group for hydrogen bonding with the urethane N–H group. The magnitude of these interactions can be measured by FTIR spectroscopy.

Fig. 9 shows the IR spectra, in the N–H stretching region, for samples TDIBD, TC1.31 and TT2.22. The band is constituted by two contributions: the band centred at about 3300 cm^{-1}, corresponding to the associated N–H groups and a small shoulder close to 3450 cm^{-1}, due to the stretching vibration of the “free” N–H groups.

As we can see in Fig. 9, the position of the hydrogen bonded N–H stretching vibration is the same in TDIBD as in TT2.22, whereas it shifts to higher frequencies in the case of TC1.31. As stretching vibration frequencies are a function of hydrogen bonding strength, we can conclude that interactions urethane/urethane and urethane/ether are of the same magnitude [23] and urethane/ester groups interactions are weaker. This fact could be responsible for the poorer photoresistance shown by the urethane linkage in poly(ester-urethanes) when compared with poly(ether-urethanes).

4. Conclusions

When studying the photodegradation of the urethane linkage in segmented aromatic poly(ester–urethanes), a mutual stabilisation effect between the ester soft segment and the urethane hard segment has been found. The extent of this stabilisation effect is related to the polymer physical state, being more prevalent when the hard/soft segment phase mixing is higher. Both, phase mixing and urethane photodegradation extent are mainly affected by soft segment molecular weight. Phase mixing is higher in low molecular weight soft segment based polymers and, therefore, the extent of the urethane linkage photodegradation is lower.

For the same hard segment concentration and soft segment molecular weight, the urethane linkages are more stable in poly(ether–urethanes) than in poly(ester–urethanes).

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