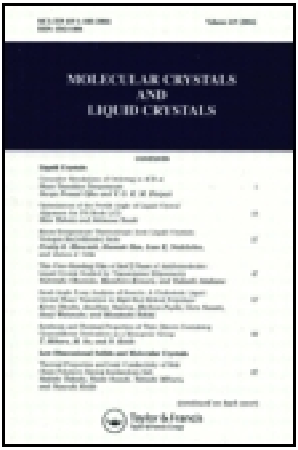

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Photochromic Effects of an Anthracene Derivative in Polyurethane

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Photochromic Effects of an Anthracene Derivative in Polyurethane

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Segmented poly(ether urethanes) with anthracene built into the hard segment based on 4,4′-diphenylmethylene diisocyanate or hexamethylene diisocyante, 1,4-butanediol, 2,6-(dihydroxymethyl)anthracene, and poly(oxytetramethylene) soft segments were synthesized. The photo-induced cycloaddition of anthracene in these polyurethanes has been studied by UV-Vis spectroscopy. A reversible change of the refractive index of polymer films could be achieved.

Keywords: anthracene; photodimerization; refractive index; segmented polyurethane

INTRODUCTION

The potential of the photochromism of anthracene derivatives [1,2] has increasingly attracted interest in connection with materials that exhibit photoswitchable properties [3]. An efficient dimerization of anthracenes is only possible if they are in a proper alignment for the interannular reaction: in a bulk polymer or solvent matrices at low temperatures [4] this may be achieved if there are little restrains of the matrix on the mobility of the anthracene moieties, or, if anthracene clustering occurs already during film formation. Referring to earlier studies of the effect of molecularly built-in nucleation agents for the crystallization of polyurethane hard segments [5,6] and the findings that suitably constituted units act as nucleation sites, this

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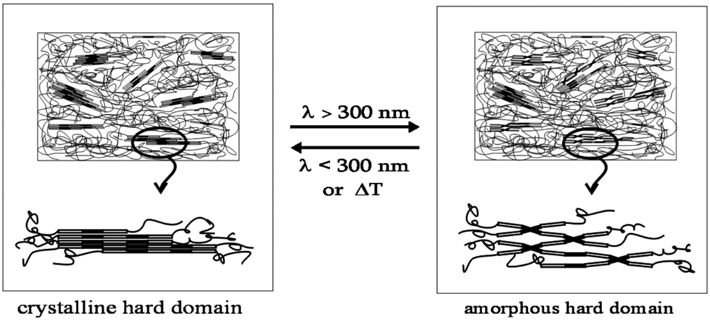


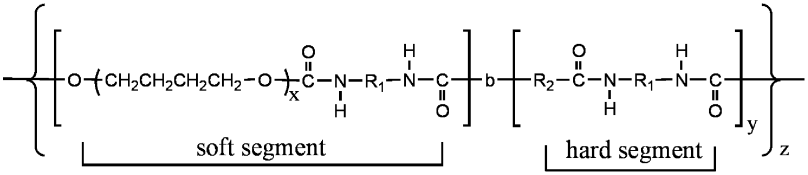
FIGURE 1 Schematic of segmented polyurethane hard domain morphology (cf. [5,6]) and anthracene dimerization induced morphology change —: hard segment containing anthracene moiety (⟷), ■: soft segment.

concept has been adapted to anthracene building blocks as nucleation moieties.

Segmented polyurethanes based on 4,4′-diphenylmethylene diisocyanate (MDI) or hexamethylene diisocyante (HDI), 1,4-butanediol (BDO) and 2,6-(dihydroxymethyl)-anthracene (DHMA), and poly (oxytetramethylene) (POTM) soft segments have been synthesized and investigated with the objective to obtain microphase separated polyurethanes with hard domains which can be reversibly switched from the crystalline to the amorphous state as schematically illustrated in Figure 1.

EXPERIMENTAL

2,6-(Dihydroxymethyl)anthracene (DHMA) was prepared via the intermediate product dimethyl 2,6-anthracenedicarboxylate (prepared according to [7]) which was reduced to the dihydroxymethyl substituted anthracene by treatment with $LiAlH_4$ (details in [8]). Segmented polyurethanes functionalized with anthracene in the hard segments were synthesized by a conventional two-step prepolymerization method in the melt. The prepolymer was obtained by reacting POTM ($M_n = 2000$, BASF) and diisocyanate (MDI or HDI; Aldrich) for 1 h at temperature T_1. The melt was chain extended with BDO and/or DHMA for 4 h at T_2. Due to the low reactivity of HDI, dibutyltin dilaurate (Aldrich) was used as a catalyst in case of HDI. The schematic structure and the composition of the polyurethanes are given in Figure 2 and Table 1.



	R_1	R_2
PU_MDI	$-C_6H_4CH_2C_6H_4-$	$-O-(CH_2)_4-O-$ / $-OCH_2AnthCH_2O-$
PU_HDI	$-(CH_2)_6-$	$-OCH_2AnthCH_2O-$

FIGURE 2 Structure of anthracene functionalized segmented polyurethanes.

TABLE 1 Chemical Composition of Segmented Polyurethanes, Reaction Temperature T_1 and T_2 of Polyurethane Synthesis, and Calculated Hard Segment (HS) and Anthracene (Anth) Content

	Molar ratio							
Polymer	POTM	Diisocyanate	BDO	Anthracene	HS (wt%)	Anth (wt%)	T_1 (°C)	T_2 (°C)
PU_MDI	1	4	2	1	41	7	80	50
PU_HDI	1	3	0	2	31	16	110	100

RESULTS AND DISCUSSION

Characterization of Segmented Polyurethanes Functionalized with Anthracene

Gel permeation chromatography (GPC) using N,N-dimethylacetamide as eluent and polystyrene calibration revealed the formation of the segmented copolymer in the chain extension reaction. The $M_{n(GPC)}$ of PU_MDI was 36000 g/mol and $M_{n(GPC)}$ of PU_HDI was 24000 g/mol, whereas that of POTM soft segment starting material was 5100 g/mol; this means that the poly(ether urethane) contains about 5–7 anthracene labelled hard segments.

Differential scanning calorimeter (DSC) analysis showed a clear soft segment glass transition temperature T_g at about -74°C (pure POTM: -85°C) indicating partial hard segment dispersion in the polyether soft phase. Further transitions were not observed in the temperature range up to about 200°C; the decomposition of the polymers begins already at this temperature region according to the thermo gravimetric analysis.

The FT-IR spectra of the segmented polyurethanes exhibited distinct absorptions of the urethane group. The carbonyl band maxima of PU_MDI appear at 1730 cm^{-1} (free carbonyl) and 1707 cm^{-1} (hydrogen bonded carbonyl) and the corresponding bands of PU_HDI at lower wave numbers, i.e. at 1720 cm^{-1} and 1690 cm^{-1}. The occurrence of hydrogen bonded carbonyls is indicative of hard domains with inter urethane hydrogen bond formation, which is particularly pronounced in the PU_HDI.

Photocycloadditive Reaction of Anthracene in Segmented Polyurethanes

The photocycloaddition and the reversibility of the reaction have been studied by UV-Vis spectroscopy. Film specimens of polymers were prepared on a quartz glass slide by casting from DMA solution. The samples were placed in a quartz glass tube and evacuated for removal of oxygen in order to prevent photooxidation during irradiation. A high pressure mercury lamp (200 W, Heraeus) was used as an excitation light source. The spectral window of 300 to 400 nm for dimerization and 200 to 300 nm for photodissociation was selected by employing interference filters.

Upon irradiation with UV light (300 to 400 nm), a decrease of the absorption peaks of anthracene around 350 nm as a function of irradiation time that is indicative of cycloaddition was observed for both polyurethanes; the assumed dimerization was faster and more complete for PU_HDI as compared to PU_MDI and it attributed to different hard segment packing. Peak increase upon shortwave UV exposure was only observed for the film sample of PU_MDI. This means that the photoinduced cycloreversion of anthracene dimerization occurred in PU_MDI only but not in PU_HDI; typical spectra are shown in Figure 3. The reversible photoreaction of PU_MDI could be repeated several times.

Photoinduced Change in Refractive Index

Refractive indices n of polymer films were determined using a prism coupler (Metricon Model 2010) equipped with a He–Ne laser light source of 632.8 nm wavelength. Measurement of refractive indices was carried out in transverse electric (TE) and transverse magnetic (TM) mode by choosing the appropriate polarization of the incident laser beam as described elsewhere [9]. The determined average refractive indices are summarized in Table 2. The direction of the observed change of the refractive indices n is in agreement with the

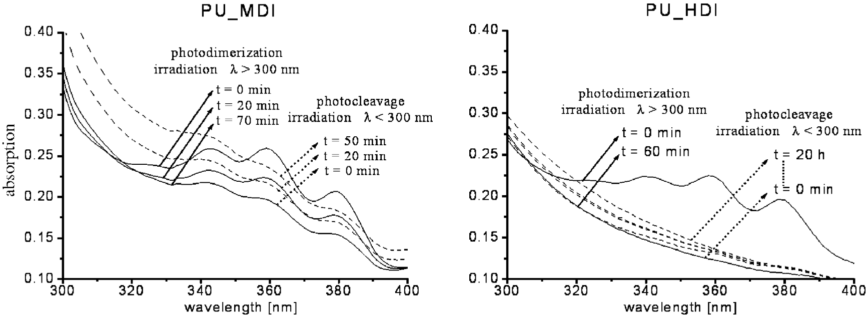


FIGURE 3 UV-spectra of anthracene functionalized segmented polyurethanes before and after irradiation.

TABLE 2 Refractive Indices of Segmented Polyurethanes: Before and After Photodimerization the Data are Average Values of at least 5 Individual Tests

Polymer	n (initial state)	n (after photodimerization)
PU_MDI	1.5206	1.5193
PU_HDI	1.4928	1.4969

photoinduced molecular changes within the polyurethanes (see Fig. 1), and the magnitude of the effect is relatively strong as compared to literature data given for other systems [3].

CONCLUSION

Segmented polyurethanes with anthracene built into the hard segment can be synthesized by using DHMA as a chain extender alone or together with, e.g., BDO. Photocycloaddition of anthracene upon irradiation at wavelengths longer than 300 nm could be achieved for both types of the polyurethanes, whereas the photodissociation with shortwave UV light was possible for PU_MDI only. The reason of the difference in the photoinduced cycloaddition and cycloreversion is not yet clear and may be related to the crystalline structure of the hard segment domain and/or photo side reactions. However, as a result of the photocycloaddition, a change of the refractive index is measured, which demonstrated the feasibility of the concept. Further investigations to elucidate the photoresponse of the PU are underway.

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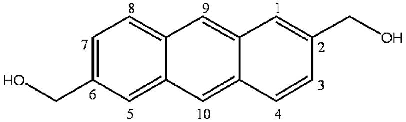
[8] Note: 1 eq. $LiAlH_4$ in THF at 0°C under argon (yellow solid, decomposition at 270°C, 99% yield). ^{1}H NMR (250 MHz, DMSO-d_6) δ 8.48 (s, 2H, Ar$-H_{9,10}$), 8.02 (d, 2H, Ar$-H_{4,8}$, J = 10 Hz), 7.94 (s, 2H, Ar$-H_{1,5}$), 7.44 (d, 2H, Ar$-H_{3,7}$, J = 10 Hz), 5.38 (s, 2H, $-$OH), 4.68 (s, 4H, $-CH_2$). ^{13}C NMR (63 MHz, DMSO-d_6) δ 139.7, 131.2, 131.0, 128.1, 125.7, 125.6, 124.2, 63.4 ($-CH_2OH$).



DHMA

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