Polymer Bulletin 27, 637–644 (1992)

Polymer Bulletin

Langmuir-Blodgett-films of photochromic polyglutamates

II. Synthesis and spreading behaviour of photochromic polyglutamates with alkylspacers and -tails of different length*

H. Menzel, B. Weichart, and M. L. Hallensleben**

Institut für Makromolekulare Chemie, Universität Hannover, Am Kleinen Felde 30, W-3000 Hannover 1, Federal Republic of Germany

Summary

Polyglutamates bearing azobenzene derivatives covalently bound to the main chain via spacers and equipped with alkyl tails of different length have been synthesized. In the polymers the chromophore can be isomerized to high extent by irradiation with UV-light. The polymers can be spread on a LANGMUIR trough. The spreading behaviour is different for irradiated and non irradiated samples, indicating a different arrangement depending on the content of cis-isomer. The films are less stable for longer spacers and smaller tails, caused by the better interaction of the azobenzene groups due to the greater mobility and minor hindrance.

Introduction

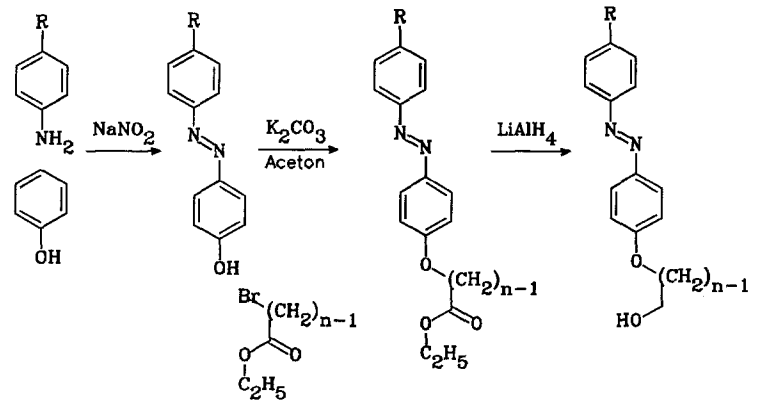
LB-films of photochromic polyglutamates have been proposed for optical data storage /1-2/. The LB-films of these "hairy rods" exhibit high thermal and mechanical stability and concomitantly great homogeneity /3-6/. First attempts to obtain materials suited for data storage were made with long alkyl chain bearing polyglutamates in mixtures with oleophilic dyes. In the LB-film the dye is dissolved in the side chain region /7/. To enhance stability and homogeneity of the photochromic LB-films, the dye has to be bound covalently to the backbone. Copolymers bearing azobenzene moieties and long alkyl chains were synthesized and investigated /8/. Although it is possible to obtain very homogeneous LB-films from these copolymers and the chromophore can be isomerized to high extent, is was not possible to produce a readable pattern by irradiation of these films /8/. The main problem might be the relatively low dye content. Therefore unipolymers bearing azobenzene derivatives with alkyl chains have been synthesized. In order to optimize the spreading behaviour alkyl chains of different length were used as spacer and tail.

Synthesis

The azobenzene derivatives were synthesized using standard methods (scheme 1).
The alcoholysis of the N-protected cyclic anhydride of the L-glutamic acid with the azobenzene containing alcohols selectively yielded the 5-ester of the L-glutamic acid. After removal of the protecting group the amino acids were treated with phosgene to obtain the N-carboxyanhydride (NCA). The NCAs were polymerized in THF using triethylamine as initiator /9/ (scheme 2). The polymers were characterized by means of ^{1}H-NMR, IR, GPC and DSC.

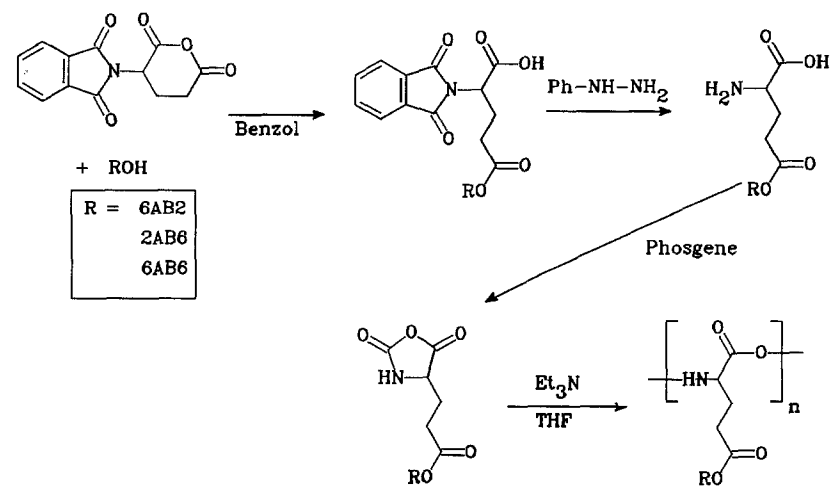
*Part I: see [8]

**To whom offprint requests should be sent



Symbol	R	n
6AB2	C6	2
2AB6	C2	6
6AB6	C6	6

Scheme 1: Synthesis of the azobenzene derivatives



Scheme 2: Synthesis of the polyglutamates via alcoholysis of N-protected cyclic anhydride of glutamic acid and the N-carboxyanhydride

Results and Discussion

UV-Vis-Spectroscopy

In solutions of all three polymers the trans-azobenzene group can be isomerized to high extent to the more polar cis-isomer by means of UV-irradiation. Irradiation with visible light causes cis to trans isomerization. Table 1 shows the content of cis-isomer in the different photostationary states as determined from the spectra using the method of FISCHER /10/.

Table.1: Cis-content of solutions of the polymers in $CHCl_3$ (c = 5.0 - 7.5 · 10^{-5} mol · l^{-1} azogroups) for the different photostationary states as determined using the method of FISCHER /10/.

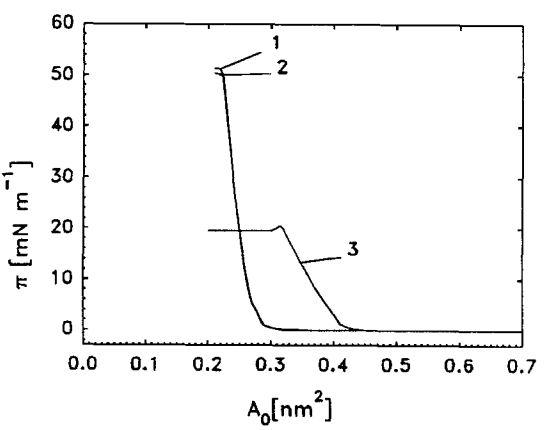
Polymer	dark adapted	cis-photostat.	trans-photostat.
P6AB2LG	0%	92%	10%
P2AB6LG	0%	93%	10%
P6AB6LG	0%	94%	11%

Spreading Behaviour

Poly(5-(2-(4-(4-hexylphenylazo)phenoxy)ethyl)-L-glutamate (P6AB2LG)

The isotherms for P6AB2LG for the dark adapted and irradiated solutions are shown in Figure 1. The surface area per monomeric unit A_0 is 0.27 nm^2 for 0% cis-isomer, 0.27 nm^2 for 10% cis-isomer and 0.41 nm^2 for 92% cis-isomer, respectively. As higher the content of cis-isomer as higher is the area per monomeric unit.

Figure 1: π/A-isotherms for P6AB2LG spread from $CHCl_3$ solutions with different content of cis-isomer
1: 0% cis
2: 10% cis
3: 92% cis
(c = $1.69 \cdot 10^{-3}$ mol·l^{-1} azogroups)



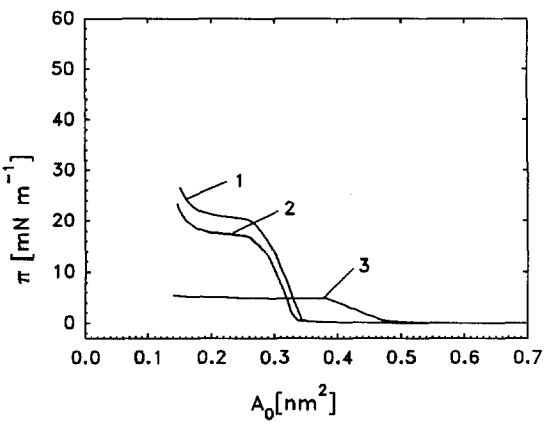
This effect can be explained by the interaction of the polar cis-isomer with the water surface, whereas the non-polar trans-isomer does not interact with water. For this reason the films with only small amounts of cis-isomer can take a more compact arrangement, in which the azobenzene group is directed towards the gas phase.

Not only the surface area, but also the height of the plateau, which can be ascribed to the formation of a bilayer and which is therefore a measure of stability of the monolayer /11,12/, depends on the cis-content of the solution used for spreading. It lowers for higher cis-contents, 51 mN · m^{-1} for the dark adapted, 50.5 mN m^{-1} for the trans- and only 19 mN m^{-1} for the cis-photostationary state.

Poly(5-(6-(4-(4-ethylphenylazo)phenoxy)hexyl)-L-glutamate (P2AB6LG)

The isotherms for P2AB6LG are shown in Figure 2. The effect of increasing the cis-content on them is qualitatively the same as described above. But the films are not as stable as those of P6AB2LG in all three states of isomerization (see table 2). For the cis-photostationary state (93% of the azogroups as cis-isomer) there is not a really stable monolayer, the collapse pressure is only 5 mN m^{-1}. For films made from dark adapted solutions of P2AB6LG the surface area per monomeric unit is larger than in the corresponding films of P6AB2LG.

Figure 2: π/A-isotherms for P2AB6LG spread form $CHCl_3$ solutions with different content of cis-isomer
1: 0% cis
2: 10% cis
3: 93% cis
(c = $1.10 \cdot 10^{-3}$ mol·l^{-1} azogroups)



Both observations can be explained taking into account the longer spacer in the P2AB6LG. The longer spacer causes a greater mobility of the azobenzene group. So even in the case of low content of cis-isomer the arrangement is not as compact as for the P6AB2LG. The greater mobility of the azobenzene group and the smaller tail in the case of P2AB6LG are responsible for the minor stability of the monomolecular film, because they ease the formation of bilayers. A portion of the energy needed to remove a molecule from the water surface /12/ can be supplied by the interaction of the azobenzene groups. For this reason the formation of bilayers is as easier as higher the mobility of the azobenzene group and as lower the steric hindrance due to larger tails.

Poly(5-(6-(4-(4-hexylphenylazo)phenoxy)hexyl)-L-glutamate (P6AB6LG)

For the P6AB6LG the isotherms are shown in Figure 3. The effect of the content of cis-isomer is again the same as described for P6AB2LG.

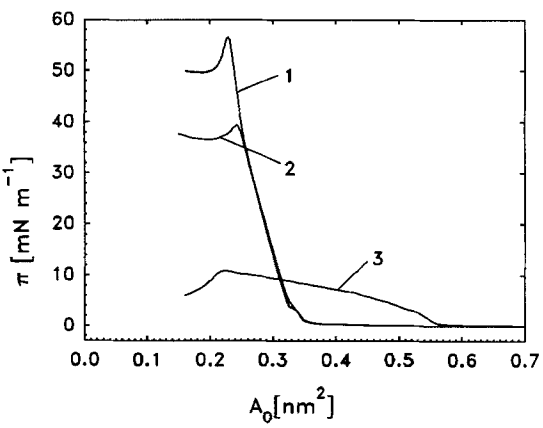
In comparison P6AB6LG shows a larger surface area per monomeric unit (see table 2). This is due to the longer side chain in this polymer, in sum 12 C-atoms in the alkyl chain in comparison to 8 C-Atoms for P6AB2LG. The stability of the films is lower than for P6AB2LG. This is caused by the greater mobility of the azogroup due to the longer

spacer. But it is higher than for the P2AB6LG because of the longer tail which hinders interaction of the azogroup while forming the bilayer.

Table 2: Surface area per monomeric unit A_0 and pressure at collapse π_c for the polymers in the different isomerization states.

	A_0 [nm^2]			π_c [mN m^{-1}]		
Polymer	dark	trans	cis	dark	trans	cis
P6AB2LG	0.27	0.27	0.41	51	50.5	19
P2AB6LG	0.34	0.33	0.48	21	18	5
P6AB6LG	0.33	0.33	0.57	50	37	11

Figure 3: π/A-isotherms for P6AB6LG spread form $CHCl_3$ solutions with different content of cis-isomer
1: 0% cis
2: 10% cis
3: 94% cis
(c = $1.06 \cdot 10^{-3}$ mol l^{-1} azogroups)



Conclusions

It is possible to obtain spreadable polymers with high content of azodye by use of alkyl chains as spacer and as tail. The stability of the monolayer depends on the length of the side chain and the position of the azobenzene group along the side chain. As longer the tail as higher is the stability due to the hindrance of interaction of the azobenzene groups in the bilayer forming process. The stability decreases with increasing mobility of the azobenzene group due to longer spacers. The most stable monolayer was obtained from the polymer with a short spacer (C_2) and a long tail (C_6).

For all polymers investigated there are great differences in the π/A-isotherms depending on the degree of isomerization. This suggests that the arrangement of the molecules in the monomolecular film is different for the different contents of cis-isomer. An irradiation of a LANGMUIR-BLODGETT-film of these polymers should therefore induce a reorientation. This reorientation should result in a pattern readable by surface plasmon microscopy in a data storage experiment /1, 13/. Investigations on the LB-films of these polymers are in progress.

Experimental

5-(4-(4-Alkylphenylazo)phenoxy)alkyl)-N-phthaloyl-L-glutamates

were synthesized according to a procedure given by FEIJEN et al. /14/. The crude products were recrystallized from ethylacetat/light petroleum (40-70°C).

5-(2-(4-(4-Hexylphenylazo)phenoxy)ethyl)-N-phthaloyl-L-glutamate:

Yield: 58% mp: 107°C

^{1}H-NMR ($CDCl_3$): δ 0.9 (T, 3H, CH_3), δ 1.3 (M, 6H, -CH_2-), δ 1.6 (M, 2H, Ph-C-CH_2), δ 2.4 - 2.8 (M, 6H, ß-CH_2, γ-CH_2, Ph-CH_2), δ 4.2 - 4.5 (M, 4H, COO-CH_2-CH_2-O-Ph), δ 4.9 - 5.1 (M, 1H, α-CH), δ 6.9 - 7.3 (M, 4H, aromatic, o position to N_2-group), δ 7.7 - 7.9 (M, 8H, aromatic, m position to N_2-group, phthaloyl group), δ 8.2 (S, 1H, COOH)

IR (KBr): 2930, 2910, 2830 cm^{-1}, 1760 cm^{-1}, 1680 cm^{-1}, 830 cm^{-1}, 720 cm^{-1}

5-(6-(4-(4-Ethylphenylazo)phenoxy)hexyl)-N-phthaloyl-L-glutamate:

Yield: 82% mp: 119°C (soften), 127°C (melting)

^{1}H-NMR ($CDCl_3$): δ 0.9 - 2.0 (M, 11H, -CH_3, -CH_2-), δ 2.1 - 2.8 (M, 6H, Ph-CH_2, ß-CH_2, γ-CH_2), δ 3.95 - 4.05 (M, 4H, COO-CH_2, CH_2-O-Ph), δ 4.9 - 5.1 (M, 1H, α-CH), δ 6.85 - 6.95 (M, 2H, aromatic, o position to OR-group), δ 7.2 - 7.3 (M, 2H, aromatic, o position to C_2H_5-group), δ 7.7 - 7.75 (M, 8H, aromatic, m-position to N_2-group, phthaloyl group)

IR (KBr): 3240 cm^{-1}, 2910, 2840 cm^{-1}, 1740 cm^{-1}, 1710 cm^{-1}, 1685 cm^{-1}, 830 cm^{-1}, 720 cm^{-1}

5-(6-(4-(4-Hexylphenylazo)phenoxy)hexyl)-N-phthaloyl-L-glutamate:

Yield: 79% mp: 111°C

^{1}H-NMR ($CDCl_3$ + 10 vol% TFA): δ 0.7 - 1.1 (M, 3H, -CH_3), δ 1.1 - 2.1 (M, 16H, -CH_2-), δ 2.4 - 2.9 (M, 6H, Ph-CH_2, ß-CH_2, γ-CH_2), δ 4.0 - 4.4 (M, 4H, COO-CH_2, CH_2-O-Ph), δ 4.9 - 5.3 (M, 1H, α-CH), δ 7.0 - 8.4 (M, 13H, aromatic, COOH)

IR (KBr): 3260 cm^{-1}, 2925, 2860 cm^{-1}, 1730 cm^{-1}, 1600 cm^{-1}, 835 cm^{-1}, 720 cm^{-1}

5-(4-(4-Alkylphenylazo)phenoxy)alkyl)-L-glutamic acids

The deblocking was carried out following a method of FEIJEN et al. /14/.

5-(2-(4-(4-Hexylphenylazo)phenoxy)ethyl)-L-glutamate:

Yield: 43% mp: 166°C (soften), 171°C (decomposition)

^{1}H-NMR (TFA-d_1): δ 0.85 (T, 3H, -CH_3), δ 1.4 (M, 6H, -CH_2-), δ 1.8 (M, 2H, Ph-C-CH_2), δ 2.4 - 3.0 (M, 6H, ß-CH_2, γ-CH_2, Ph-CH_2), δ 4.55 - 4.7 (M, 5H, COO-CH_2-CH_2-O-Ph, α-CH), δ 7.4 - 8.5 (M, 8H, aromatic)

IR (KBr): 3010 cm^{-1}, 2940, 2900, 2830 cm^{-1}, 1710 cm^{-1}, 1650, 1590 cm^{-1}, 840 cm^{-1}

5-(2-(4-(4-Ethylphenylazo)phenoxy)hexyl)-L-glutamate:

Yield: 60% mp: 183-188°C

^{1}H-NMR (TFA-d_1): δ 0.9 (M, 3H, -CH_3), δ 1.3 (M, 6H, -CH_2-), δ 1.8 (M, 2H, Ph-C-CH_2), δ 2.4 - 3.0 (M, 6H, Ph-CH_2, ß-CH_2, γ-CH_2), δ 4.5 (M, 5H, COO-CH_2, CH_2-O-Ph, α-CH), δ 7.4 - 8.5 (M, 8H, aromatic)

IR (KBr): 2920, 2840 cm^{-1}, 1710 cm^{-1}, 1610 cm^{-1}, 840 cm^{-1},

5-(6-(4-(4-Hexylphenylazo)phenoxy)hexyl)-L-glutamate:

Yield: 60% mp: 187°C (decomposition)

^{1}H-NMR ($CDCl_3$ + 15 vol% TFA): δ 0.7 - 1.1 (M, 3H, -CH_3,), δ 1.1 - 2.2 (M, 16H, -CH_2-), δ 2.4 - 2.9 (M, 6H, Ph-CH_2, ß-CH_2, γ-CH_2), δ 4.0 - 4.6 (M, 5H, α-CH, COO-CH_2, CH_2-O-Ph), δ 7.0 - 8.3 (M, 11H, aromatic, COOH, -NH_3^+)

IR (KBr): 2930, 2860 cm^{-1}, 1730 cm^{-1}, 1605 cm^{-1}, 1585 cm^{-1}, 840 cm^{-1}

5-(4-(4-Alkylphenylazo)phenoxy)alkyl)-L-glutamic acid-N-carboxyanhydride

The NCAs were synthesized according to a general procedure given by GOODMMAN et al. /15/. The products were purified by recrystallization (several times) from anhydrous ethylacetat/light petroleum (40-70°C), but it was not possible to remove all hydrochloric acid because the azo group can be protonated easily.

5-(2-(4-(4-Hexylphenylazo)phenoxy)ethyl)-L-glutamic-N-carboxyanhydride:

Yield: 93% mp: 189°C (decomposition)

^{1}H-NMR ($CDCl_3$): δ 0.9 (T, 3H, $-CH_3$), δ 1.3 (M, 6H, $-CH_2-$), δ 1.7 (M, 2H, Ph-C-CH_2), δ 2.2 - 2,5 (M, 6H, ß-CH_2, γ-CH_2, Ph-CH_2), δ 4.5 (M, 5H, COO-CH_2-CH_2-O-Ph, α-CH), δ 6.9 - 7.3 (M, 4H, aromatic, o position to N_2-group), δ 7,7 - 8.1 (M, >4H, aromatic, m position to N_2-group, protonated azogroup)

IR (KBr): 2940, 2910, 2840 cm^{-1}, 1840 cm^{-1}, 1770 cm^{-1}, 1710, 840 cm^{-1}

5-(6-(4-(4-ethylphenylazo)phenoxy)hexyl)-L-glutamic-N-carboxyanhydride:

Yield: 96% mp: 125°C (decomposition)

^{1}H-NMR ($CDCl_3$): δ 1.0 - 3.0 (M, 17H, $-CH_3$, $-CH_2-$, Ph-CH_2, ß-CH_2, γ-CH_2) δ 3.8 - 4.5 (M, 5H, α-CH, COO-CH_2, CH_2-O-Ph), δ 6.3 (S, 1H, N-H broad), δ 6.8 - 8.1 (M, >8H, aromatic, protonated N_2-group)

IR (KBr): 3330 cm^{-1}, 2940, 2870 cm^{-1}, 1880 ,1790, 1710 cm^{-1}, 1605, 1585 cm^{-1}, 845 cm^{-1}

5-(6-(4-(4-hexylphenylazo)phenoxy)hexyl)-L-glutamic-N-carboxyanhydride:

Yield: 80% mp: 110°C (decomposition)

^{1}H-NMR ($CDCl_3$): δ 0.7 - 3.0 (M, 25H, $-CH_3$, $-CH_2-$, Ph-CH_2, ß-CH_2, γ-CH_2) δ 3.9 - 4.5 (M, 5H, α-CH, COO-CH_2, CH_2-O-Ph), δ 6.3 (S, 1H, N-H broad), δ 6.8 - 8.1 (M, >8H, aromatic, protonated N_2-group)

IR (KBr): 3360 cm^{-1}, 2940, 2870 cm^{-1}, 1880, 1730 cm^{-1}, 1605, 1585 cm^{-1}, 840 cm^{-1}

Polymerizations

Polymerizations were carried out as described before /9/.

Poly-(5-(2-(4-(4-hexylphenylazo)phenoxy)ethyl)-L-glutamate):

Yield: 67%

^{1}H-NMR (TFA-d_1): δ 1.0 (3H, $-CH_3$), δ 1.5 (6H, $-CH_2-$), δ 1.9 (2H, Ph-C-CH_2, broad), δ 2.5 (2H, ß-CH_2, broad), δ 2.9 (4H, γ-CH_2, Ph-CH_2, broad), δ 4.7 (5H, COO-CH_2-CH_2-O-Ph, α-CH, broad), δ 7.3 -8.5 (8H, aromatic)

IR (film cast from $CHCl_3$): 3270 cm^{-1}, 3020 cm-1, 2900, 2830 cm^{-1}, 1720 cm-1, 1640 cm^{-1}, 840 cm^{-1}

GPC: The polymer possesses a broad bimodal molecular weight distribution.

DSC: Between 0°C and 150°C are no phase transitions detectable. mp: 210°C (decomposition)

Poly-(5-(6-(4-(4-ethylphenylazo)phenoxy)hexyl)-L-glutamate):

Yield: 15%

^{1}H-NMR ($CDCl_3$): δ 0.6 - 2.2 (13H, $-CH_3$, $-CH_2-$, ß-CH_2), δ 2.2 - 3.2 (M 4H, Ph-CH_2, γ-CH_2, broad), δ 3.2 - 5.0 (M, 5H, Ph-O-CH_2, CH_2-OOC, α-CH, broad), δ 6.5 - 8.1 (M, 9H, aromatic, -NH-)

IR (KBr): 3300 cm^{-1}, 2940, 2870 cm^{-1}, 1730, 1660 cm^{-1}, 1600 cm^{-1}, 840 cm^{-1}

GPC: The polymer possesses a broad molecular weight distribution.

DSC: The polymer exhibits exothermic transitions at 133°C and 193°C.

Poly-(5-(6-(4-(4-hexylphenylazo)phenoxy)hexyl)-L-glutamate):

Yield: 16%

^{1}H-NMR ($CDCl_3$): δ 0.6 - 2.0 (23H, $-CH_3$, $-CH_2-$, Ph-CH_2, ß-CH_2, γ-CH_2), δ 2.1 - 3.2 (M, 3H, Ph-CH_2, α-CH, broad), δ 3.2 - 4.7 (M, 4H, Ph-O-CH_2, CH_2-OOC, broad), δ 6.5 - 8.0 (M, 9H, aromatic, -NH-)

IR (KBr): 3300 cm^{-1}, 2930, 2860 cm^{-1}, 1730, 1660 cm^{-1}, 1600 cm^{-1}, 835 cm^{-1}

GPC: The polymer possesses a broad molecular weight distribution.

DSC: The polymer possesses a glass transition at 166°C.

Instruments and Methods

^{1}H-NMR spectra were recorded with a Bruker WP 80 SY instrument. IR spectra were recorded on a Perkin-Elmer 398 instrument. The thermograms were obtained with a Perkin-Elmer DSC 2a. UV spectra were recorded on a Perkin-Elmer Lambda 5 instrument. The content of cis-isomer was determined using the method of FISCHER /10/.

Irradiations were carried out with a 125 W high pressure mercury lamp (Phillips HPK 125), employing a cut off filter to obtain light with a wavelength $\lambda > 470$ nm (DEMA FW-161) and a band pass filter for light with $\lambda = 360 \pm 50$ nm (DEMA UVW-55).

The copolymers were spread from $CHCl_3$. The concentrations were 0.3 - 0.5 g/l. The solutions were kept in the dark for at least one week to ensure full trans-configuration or were irradiated for at least 30 min for photostationary state. The solutions were handled under red light conditions. A Lauda FW 1 trough filled with "Milli-Q" water was used recording the surface pressure / surface area isotherms. The velocity of the barrier was 0.9 cm/min. A period of at least 20 min was between spreading and compression of the film. The area per monomeric unit A_0 was determined by extrapolating the linear portion of the isotherm to zero pressure.

Acknowledgements

Financial support by the *Deutsche Forschungsgemeinschaft* is gratefully acknowledged.

Literature

/ 1/ W. Hickel, G. Duda., G. Wegner, W. Knoll, Makromol. Chem., Rapid Commun. 10, 353 (1989)
/ 2/ M. Sawodny, A. Schmidt, C. Urban, H. Ringsdorf, W. Knoll, Makromol. Chem., Macromol. Symp. 46, 217 (1991)
/ 3/ G. Duda, A.J. Schouten, T. Arndt, G. Lieser, G.F. Schmidt, C. Bubeck, G. Wegner, Thin Solid Films 159, 221 (1988)
/ 4/ E. Orthmann, G. Wegner, Makromol. Chem., Rapid Commun. 7, 243 (1986)
/ 5/ E. Orthmann, G. Wegner, Angew. Chem. Int. Ed. Eng. 25, 1105 (1986)
/ 6/ F. Embs, D. Funhoff, A. Laschewski, U. Licht, H. Ohst, W. Prass, H. Ringsdorf, G. Wegner, R. Wehrmann, Adv. Mater. 3, 25 (1991)
/ 7/ G. Duda, G. Wegner, Makromol. Chem., Rapid Commun. 9, 495 (1988)
/ 8/ H. Menzel, M.L. Hallensleben, Polym. Bull. 27, 89 (1991)
/ 9/ M.L. Hallensleben, H. Menzel, Br. Polym. J. 23, 199 (1990)
/10/ E.J. Fischer, J. Phys. Chem. 71, 3704 (1967)
/11/ F. Takeda, M. Matsumoto, T. Takenaka, Y. Fujiyoshi, J. Coll. Interf. Sci. 84, 220 (1981)
/12/ B.R. Malcom, Proc. R. Soc. London, Ser. A 305, 363 (1968)
/13/ J.P. Rabe, Adv. Mater. 2, 100 (1990)
/14/ J. Feijen, W.L. Sederel, K. DeGroot, A.C. DeVisser, A. Bantjes, Makromol. Chem. 175, 3193 (1974)
/15/ W.D. Fuller, M.S. Verlander, M. Goodmann, Biopolymers 15, 1869 (1976)

Accepted October 31, 1991 C