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# $Trans \rightarrow Cis$ Photoisomerization of the Stilbene Residues in the Side Chains of Copolymers from 2-Hydroxyethyl Methacrylate and Monomer Containing Stilbene Residue

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#### SUMMARY:

The rate of the *trans* $\rightarrow$ *cis* photoisomerization of the stilbene residue was compared in the copolymer 3 from 2-hydroxyethyl methacrylate (1) and trans-N-4-(4-nitrostyryl)phenylmethacrylamide (2a) with its low molecular weight analogue trans-N-4-(4-nitrostyryl)phenylisobutyramide (2b) in methanol, 2-ethoxyethanol and in the binary solvents propanol/water and tert-butyl alcohol/water. It was observed that the trans→cis photoisomerization of the stilbene residues was more rapid at 20°C in the side chains of the copolymer than for 2b in most solvents. This result may be interpreted on the basis of the quantum yield dependence for the  $trans \rightarrow cis$  isomerization on the polarity of the medium where the isomerization takes place. Acceleration of the  $trans \rightarrow cis$  isomerization of the stilbene residues in the side chains of the copolymer results from a decrease in the polymer microenvironment polarity as compared to the polarity of the solvent itself. This interpretation is supported by direct measurement of the polarity of the polymer chain microenvironment, based on the Kosower semi-empirical polarity scale. The course of the *trans* $\rightarrow$ *cis* isomerization of **2b** and **3** does not obey the equilibrium, first-order reaction for all the solvents mentioned. The effect of preferential sorption of one of the components in binary solvents on the polymer coil and the effect of temperature on the photochemical  $trans \rightarrow cis$  isomerization are discussed in connection with the experimental results.

# ZUSAMMENFASSUNG:

Es wurde die Geschwindigkeit der  $trans \rightarrow cis$  Photoisomerisierung des Stilbenrestes im Copolymeren 3 aus 2-Hydroxyäthylmethacrylat (1) und trans-N-4-(4-nitrostyryl)phenylmethacrylamid (2a) einerseits mit derjenigen in dem niedermolekularen Analogon des letzteren, trans-N-4-(4-nitrostyryl)phenylisobutyramid (2b) andererseits, in Methanol, 2-Äthoxyäthanol und in den binären Lösungsmitteln Propanol/Wasser und tert-Butylalkohol/Wasser verglichen. Dabei wurde beobachtet, daß die  $trans \rightarrow cis$  Photoisomerisierung des Stilbenrestes in den Seitenketten des Copolymeren bei 20°C in den meisten Lösungsmitteln schneller als beim 2b verläuft. Dieses Ergebnis kann auf der Grundlage der

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Abhängigkeit der Quantenausbeute der  $trans \rightarrow cis$  Isomerisierung von der Polarität des Milieus, in dem die Isomerisierung verläuft, interpretiert werden. Die Beschleunigung der  $trans \rightarrow cis$  Photoisomerisierung der Stilbenreste in den Seitenketten des Copolymeren wird durch ein Absinken der Polarität des Mikromilieus des Polymeren im Vergleich zur Polarität des Lösungsmittels selbst verursacht. Diese Interpretation stützt sich auf die direkte Messung der Polarität des Mikromilieus der Polymerkette auf der Grundlage der Kosowerschen semi-empirischen Polaritätsskala. Der Verlauf der  $trans \rightarrow cis$  Isomerisierung von **2b** und **3** gehorcht nicht der Gleichgewichtsreaktion erster Ordnung für alle erwähnten Lösungsmittel. Der Einfluß der Vorzugssorption einer der Lösungsmittelkomponenten in binären Lösungsmitteln auf das Polymerknäuel und der Einfluß der Temperatur auf die photochemische  $trans \rightarrow cis$  Isomerisierung werden im Zusammenhang mit den experimentellen Ergebnissen diskutiert.

# Introduction

Reactions of functional groups in a polymer are studied for the following two prevalent reasons: to obtain a modified polymer or to study certain physical-chemical interactions of the polymer by means of an investigation of the rates and mechanisms of chemical reactions, in which these groups are involved.

The effect of the polymer molecule on the isomerization of the azobenzene moiety in either the backbone or a side chain has been studied by comparing the isomerization rates of these polymers with those of the corresponding low-molecular weight model compounds. Copolymers of various vinylazobenzenes<sup>1</sup>, *N*-(4-phenylazo)phenylmethacrylamide and *N*-(4-phenylazo)phenyl-acrylamide<sup>2</sup> with various monomers show, similarly to simple aromatic azocompounds, photochromism<sup>3</sup>. Polyamides with azobenzene residues in their backbone and analogous model compounds were used to study the rates of the conformation changes<sup>4,5</sup>. Other polymers containing photochromic units were also studied<sup>6</sup>. The photochemical isomerization of chrysophenine sorbed on a swelled 2-hydroxyethylmethacrylate/ethylene dimethacrylate polymer gel results in a change of the gel volume and the water absorption<sup>7</sup>.



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We studied the  $trans \rightarrow cis$  photoisomerization of stilbene residues in side chains of copolymers from 2-hydroxyethyl methacrylate (1) with trans-N-4-(4nitrostyryl)phenylmethacrylamide (2a). We attempted to express semiquantitatively the contribution of the polymer chain to changes in the behavior of bound stilbene as compared to the low-molecular weight analogue.

# Results and Discussion

Polymerization and copolymerization of *trans-N-4-(4-nitrostyr-yl)* phenylmethacrylamide (**2a**)

The copolymerization of 2a with 1 was carried out in DMF solution. For the compositions of the polymerization mixtures and of the copolymers see Tab. 1. The compositions were calculated from the nitrogen content

Mole fraction of <b>2a</b> in monomer feed	Mole fraction of <b>2a</b> in copolymer		
f	$F^{a}$	<i>F</i> <sup>b)</sup>	
0,0505°)	0,0250	0,0258	
0,0504	0,0213	0,0212	
0,0996°)	0,0431		
0,197	0,136	0,138	
0,3019	0,233	0,228	
0,5000	0,393	0,391	
0,6700	0,562		
0,8021	0,713		
0,9063	0,855		
1,0	trace polymer amount		

Tab. 1. Copolymerization of *trans-N*-4-(4-nitrostyryl)phenylmethacrylamide (**2a**) with 2-hydroxyethyl methacrylate (**1**). Conc. of comonomers 0,5 mol/l in DMF; mole fraction of 2,2'-azoisobutyronitrile 0,002; polymerization temperature  $60 \,^{\circ}\text{C}$ 

<sup>a)</sup> Based on elemental analysis.

<sup>b)</sup> Based on spectrophotometry in CH<sub>3</sub>OH.

<sup>c)</sup> Data omitted for calculating monomer reactivity ratios because of too high conversion.

resulting from elemental analysis, and spectroscopically by evaluation of the absorption for the stilbene unit at  $\lambda_{max, trans}$ . A good agreement between the copolymer compositions obtained from the two determinations demonstrated that the absorption coefficient  $\varepsilon_{\lambda_{max, trans}}$  of the stilbene unit in the copolymer is about the same as  $\varepsilon_{\lambda_{max, trans}}$  of the low-molecular weight analogue

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*trans-N*-4-(4-nitrostyryl)phenylisobutyramide (2b), which also suggests that 2a underwent the copolymerization similarly to the other methacrylic acid derivatives with no other side reactions appearing. The calculation of the monomer reactivity ratios was based on the data summarized in Tab. 1 and carried out by the method of Fineman and Ross<sup>8)</sup> and the non-linear regression method according to Tidwell and Mortimer<sup>9)</sup> (Tab. 2). The statistical

Tab. 2. Monomer reactivity ratios trans-N-4-(4-nitrostyryl) phenylmethacrylamide (2a) with 2-hydroxyethyl methacrylate (1)

	Fineman-Ross	Tidwell	Tidwell-Mortimer	
r <sub>2a</sub>	<i>r</i> <sub>1</sub>	r <sub>2a</sub>	ri	
0,62±0,02	1,72±0,14	0,597	1,46	

distribution of the monomeric units in the copolymer was calculated according to Harwood<sup>10)</sup>. The copolymer **3** from **1** and **2a** used for the photochemical isomerization was characterized by the following triad fractions with monomeric units **B** in the center: 0,011, 0,0634 and 0,9455 for the triads: **BBB**, **BBA** and **ABA**, resp. The copolymers of **1**, 2-vinylpyridine (2-VP), and 4-vinylpyridine (4-VP) with 4-(3-ethoxy-4-hydroxystyryl)-1-(2-methacryloyl-oxyethyl)pyridinium chloride (4) used for the solvatochromic measurements contained about 0,05 mole-% monomeric units from **4** (mole fraction  $5 \cdot 10^{-4}$ , determined spectrophotometrically).



Photochemical trans-cis isomerization of trans-N-4-(4-nitrostyryl)phenylisobutyramide (**2b**) and of the copolymer of trans-N-4-(4-nitrostyryl)phenylmethacrylamide (**2a**) with 2-hydroxyethyl methacrylate (**1**)

The rate of the photochemical  $trans \rightarrow cis$  isomerization of the copolymer **3** was studied and compared with the rate of the photochemical  $trans \rightarrow cis$  isomerization of **2b** as a model compound. Tab. 3 summarizes absorption maxima of the copolymer **3** and of the model compound **2b** in various solvents. Spectra of the copolymer **3** and of **2b** in the region of wavelengths corresponding to the absorption of *trans*- and *cis*-isomers are mutually very

Solvent	Copolymer <b>3</b>		Model compound <b>2b</b>	
	$\lambda_{\rm max}/{\rm nm}$	10 <sup>-4</sup> ·Eżmax. trans	$\lambda_{max}/nm$	$10^{-4} \cdot \varepsilon_{\lambda_{\max, trans}}$
Methanol	368	2,75	370	2,78
2-Ethoxy-				
ethanol	375	2,71	380	2,68
Propanol/wat	er <sup>a)</sup>			
(0,80)	373	2,72	375	2,74
(0,50)	374	2,71	376	2,68
(0,30)	374	2,70	377	2,71
tert-Butyl alco	ohol/water <sup>a)</sup>			
(0,95)	370	2,70	375	2,72
(0,90)	372	2,66	376	2,68
(0,80)		_	376	2,72
(0,75)	372	2,68		
(0,70)			377	2,68
(0,60)	373	2,70	377	2,72
(0,45)	373	2,71	377	2,69
(0,30)	374	2,68	378	2,70
Isopropyl alco	ohol <sup>b)</sup>			
	368	2,72	370	2,75

Tab. 3. Absorption maxima and molar absorption coefficients of the copolymer 3 from *trans-N*-4-(4-nitrostyryl)phenylmethacrylamide (2a) and 2-hydroxyethyl methacrylate (1) and of the model compound *trans-N*-4-(4-nitrostyryl)phenylisobutyramide (2b)

<sup>a)</sup> Numbers in parentheses denote volume fractions of the corresponding alcohol.
<sup>b)</sup> 40°C.

similar. The molar absorption coefficients at the wavelength  $\lambda_{max}$  for the *trans*- and *cis*-isomers of the model compound and of the copolymerized monomer **2a** in the same solvents are therefore almost identical.

Compounds containing stilbene groups, when exposed to irradiation of an appropriate wavelength, show both  $trans \rightarrow cis$  and  $cis \rightarrow trans$  isomerization. The isomerization may be followed spectrometrically, based on the change of the optical density D in the region of the *trans*- or *cis*-isomer absorption. The reaction is characterized by the photostationary state; the photostationary state composition of the *cis*- and *trans*-stilbene isomers depends on the wavelength of the radiation used, on the molar absorption coefficients of the *trans*- and *cis*-isomers at this wavelength and on the photoisomerization quantum yield  $\Phi_t$  (*trans \rightarrow cis*) and  $\Phi_c$  (*cis \rightarrow trans*) of the photoisomerization. Fischer *et al.*<sup>11)</sup> and Schulte-Frohlinde *et al.*<sup>12)</sup> studied the photoisomerization of stilbene disubstituted with electron donor and acceptor groups in the 4 and 4' positions (4-methoxy-4'-nitrostilbene and 4-dimethylamino-4'-nitrostilbene) at various temperatures, in different solvents of different polarity. They found that  $\Phi_t$  dropped with increasing solvent polarity while  $\Phi_c$  was independent of solvent polarity.

In the present study the isomerization was studied in methanol, 2-ethoxyethanol and in the mixtures *tert*-butyl alcohol/water and propanol/water. The dependence of the optical density of the dissolved copolymer and model compound on the time of exposure to the light was studied. It was found that at 20 °C the copolymer underwent isomerization in methanol and 2-ethoxyethanol with a higher rate as compared to the model compound (Fig. 1, data for methanol are not included for simplicity's sake). The higher rate of the *trans* $\rightarrow$ *cis* isomerization results from a lower microenvironment polarity



Fig. 1. Photochemical trans $\rightarrow$  cis isomerization of the copolymer 3 from 2-hydroxyethyl methacrylate (1) and trans-N-4-(4-nitrostyryl)phenylmethacryl-amide (2a) and of the model compound trans-N-4-(4-nitrostyryl)phenylisobutyr-amide (2b) in 2-ethoxyethanol. D: optical density; 3:  $\odot$ , 20°C;  $\bullet$ , 60°C; 2b:  $\triangle$ , 20°C;  $\bigstar$ , 60°C

of the polymer chain as compared to the polarity of the solvents used. The microenvironment polarity of the poly(2-hydroxyethyl methacrylate) chain is affected by the non-polar contribution of the polymer chain itself. The isomerization of the copolymer 3 in methanol is slower than that in 2-ethoxyethanol. Similar to this, the model compound 2b shows faster isomerization in 2-ethoxyethanol than in methanol. The microenvironment polarity of the polymer chain is higher in methanol than in 2-ethoxyethanol. An interesting course of the isomerization can be observed at 60°C (s. Fig. 1): In 2-ethoxyethanol isomerization rate of the model compound 2b is enhanced at 60 °C. The increase in the *trans* $\rightarrow$ *cis* isomerization rate occurs as a result of an increase of the photoisomerization quantum yield  $\Phi_t$  of the model compound **2b** with the temperature, similar to the other 4,4'-disubstituted stilbenes<sup>11)</sup>. The polymer isomerization rate is the same at both temperatures, 20°C and 60°C. The effect of the polymer isomerization quantum yield  $(\Phi_t)_3$  namely an increase at higher temperature, is probably compensated by an increase in the polymer chain microenvironment polarity which results from an increased intermolecular interaction polymer-solvent. The model compound showed the same behavior in 2-ethoxyethanol and in methanol. The copolymer isomerization rate in methanol at 60°C is lower than that at 20°C. The increase in the chain microenvironment polarity resulting from the interaction polymer-solvent at the higher temperature is more important in the thermodynamically inferior solvent<sup>13,14</sup>) methanol than in 2-ethoxyethanol.

Fig. 2. Photochemical  $cis \rightarrow trans$ isomerization of trans-N-4-(4-nitrostyryl)phenylisobutyramide (**2b**) in the binary solvent tert-butyl alcohol/water.  $\Delta D_0 = D_0 - D$ ;  $\Delta D = D - D_{\infty}$ ;  $D_0$ ,  $D_{\infty}$ , D: optical densities at time t = 0, in the stationary state, and at time t; volume fraction of *tert*-butyl alcohol 0,3 ( $\bullet$ ) and 0,45 ( $\bigcirc$ )



The course of the *trans* $\rightarrow$ *cis* isomerization of the model compound **2b** does not obey the equation of the equilibrium, first-order reaction (T = *trans*-, C = *cis*-isomer):

$$T \xleftarrow{\overline{k_1}}{\overline{k_1}} C$$
$$\frac{dC}{dt} = \overrightarrow{k_1} T - \overleftarrow{k_1} C$$
(1)

The dependence  $\ln(\Delta D_0/\Delta D)$  on time  $t^{*}$  is strongly curved (see Fig. 2).

This is also true to a remarkable extent for the copolymer of interest. The largest deviations from the first-order reaction were observed for the model compound 2b in methanol, 2-ethoxyethanol, and in binary mixtures with high alcohol concentrations. By contrast to this for the HEMA-SMA copolymer 3 the largest deviations can be observed in binary solvents with low alcohol contents. The deviation from the equilibrium, first-order reaction does not result from the thermal isomerization; this was demonstrated by experiments carried out at 20°C and 60°C. Without the exposure to irradiation, the trans $\rightarrow$  cis isomerization occurs neither in the model compound **2b**, nor in the copolymer 3. In addition, the optical density of samples partially isomerized to the *cis*-isomer did not increase due to thermal  $cis \rightarrow trans$  back isomerization while heating to 20°C and 60°C in the dark for time intervals of 30, 120 and 240 min. Use of polychromatic light during the isomerization also cannot represent a reason for which the reaction does not obey the equation of a equilibrium, first-order reaction. We attempted to express the initial course of the optical density dependence on time with the help of the polynomial approximation,  $D = A + Bt + C't^2$ . In spite of the fact that this approximation cannot be supported by a physical-chemical interpretation,

\*) Eq. (1) for the equilibrium, first-order reaction was adjusted as to obtain Eq. (2)

$$\frac{\mathrm{d}\Delta \mathrm{T}}{\Delta \mathrm{T}} = -(\overrightarrow{k_1} + \overleftarrow{k_1}) \cdot \mathrm{d}t \tag{2}$$

where  $\Delta T = T - T_R$  (T<sub>R</sub> is the *trans*-isomer concentration in the photostationary state).

$$D = \varepsilon_{\rm c} \cdot l \cdot {\rm C} + \varepsilon_{\rm t} \cdot l \cdot {\rm T} \tag{3}$$

where  $\varepsilon_t$  and  $\varepsilon_c$  are the molar absorption coefficients of the *trans*- and *cis*-isomers, resp. By substitution from Eq. (3) we obtain for l=1 cm after rearrangement

$$\Delta D = (\varepsilon_{\rm t} - \varepsilon_{\rm c}) \cdot \Delta T \tag{4}$$

where  $\Delta D = D - D_R$  ( $D_R$  is the optical density at time  $t = \infty$ ). The combined Eqs. (2) and (4) yield after integration the following relationship:

$$\ln \frac{\Delta D_0}{\Delta D} = (\vec{k_1} + \vec{k_1}) \cdot t \tag{5}$$

where  $\Delta D_0 = D_0 - D_R$  ( $D_0$  is the optical density at time t = 0).

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the initial rate of the *trans* $\rightarrow$ *cis* isomerization may be expressed as  $(\varepsilon_c - \varepsilon_t) \cdot V_i^{*}$  and thus individual systems in which the isomerization occurs may be compared (Tab. 4).

Certain binary solvents show for poly(2-hydroxyethyl methacrylate) a synergistic effect which is accompanied by the preferential sorption of the first or second component of the binary solvent on the polymer coil<sup>14,15</sup>. The effect of the preferential sorption on the trans $\rightarrow$  cis isomerization was studied in these systems. The isomerization rate for both, the copolymer 3 and the model compound 2b was found to drop with decreasing volume fraction of propanol or tert-butyl alcohol in the binary solvent. The rate of the copolymer *trans* $\rightarrow$ *cis* isomerization depending on the binary solvent composition is either the same or higher than that for the model compound (Fig. 3). Based on the behavior of poly(2-hydroxyethyl methacrylate) in the binary solvent propanol/water one could assume the preferential sorption of water on the polymer chain to result in such an increase of the polarity in the polymer chain domain that the copolymer  $trans \rightarrow cis$  isomerization rate will be lower than that in the case of the model compound in the same solvent. It was found that the preferential sorption of water on the polymer chain did not affect the polymer chain microenvironment polarity to such an extent which could effect a lower trans $\rightarrow$  cis isomerization rate for the copolymer than for the model compound. The backbone of the poly(2-hydroxyethyl methacrylate) affects decisively its own microenvironment polarity; it also has the decisive effect on the isomerization rate. The preferential sorption of

\*) From the polynomial approximation  $D = A + Bt + C't^2$  it follows for t = 0:

$$\frac{\mathrm{dC}}{\mathrm{d}t} = \vec{k}_1 \mathbf{T}_0 = V_\mathrm{i} \tag{6}$$

for l = 1 cm:

$$D = \varepsilon_{\rm t} \mathbf{1} + \varepsilon_{\rm c} \mathbf{C}$$
$$D = (\varepsilon_{\rm c} - \varepsilon_{\rm t}) d\mathbf{C}$$
(7)

$$\frac{\mathrm{d}D}{\mathrm{d}t} = (\varepsilon_{\mathrm{c}} - \varepsilon_{\mathrm{t}})\vec{k}_{\mathrm{1}}T_{\mathrm{0}} = (\varepsilon_{\mathrm{c}} - \varepsilon_{\mathrm{t}})\cdot V_{\mathrm{i}}$$

 $\frac{\mathrm{d}D}{\mathrm{d}t} = \mathrm{B}$ 

where  $V_i$  is the initial *trans* $\rightarrow$ *cis* photoisomerization rate and A, B, C' are the second-order polynomial coefficients.

Solvents		$ B  \cdot 10^{3}/m$	in <sup>-1</sup>		
	model compound <b>2b</b>		copoly	copolymer 3	
	20 °C	60°C	20°C	60°C	
Methanol	6,1	8,6	15,9	15,9	
2-Ethoxy-					
ethanol	12,8	18,5	15,9	15,9	
Propanol/wate	er <sup>a)</sup>				
(0,80)	17,0		17,0		
(0,50)	9,3		9,3		
(0,30)	3,9	—	5,7		
tert-Butyl alco	ohol/water <sup>a)</sup>				
(0,90)	22,4	_	23,1	_	
(0,80)	17,7				
(0,75)		_	19,8		
(0,70)	13,9	_			
(0,60)	12,1		15,5		
(0,45)	7,4	_	14,8		
(0,30)	4,4	_	10,3		

Tab. 4. Polynomial approximation of the optical density D according to  $D = A + Bt + C't^2$ (s. text)

<sup>a)</sup> Numbers in parentheses denote volume fractions of the corresponding alcohol; photoisomerization at 20 °C,  $B = (\varepsilon_c - \varepsilon_i) \cdot V_i$ .

propanol on the polymer coil which occurs in a binary solvent that contains a volume fraction of less than about 0,5 of the alcohol (propanol or *tert*-butyl



Fig. 3. Photochemical *trans*   $\rightarrow cis$  isomerization of copolymer 3 ( $\bigcirc$ ) and of the model compound 2b ( $\bullet$ ) in the sol vent mixture propanol/water. Volume fraction of propanol 0,3 (-----); 0,5 (-----) and 0,8 (-----)

alcohol) reduces the polarity of the polymer chain domain and thus also the polarity of the adjacent polymer chain microenvironment where the isomer-

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ization occurs. Owing to this, a great difference is obviously observed between the rate of the *trans* $\rightarrow$ *cis* isomerization of the copolymer and that of the model compound.



Fig. 4. Photochemical  $trans \rightarrow cis$  isomerization of copolymer 3 (O) and of model compound **2b** ( $\bullet$ ) in *tert*-butyl alcohol/water (volume fraction of *tert*-butyl alcohol 0,3). Values  $\Delta$  are read off from plot  $(D)_{2b}$  vs.  $(E_T)_5$  for  $(E_T)_6$  (s. text)

Fig. 5. Photochemical *trans* $\rightarrow$ *cis* isomerization of copolymer **3** (O) and of model compound **2b** ( $\bullet$ ) in *tert*-butyl alcohol/water (volume fraction of *tert*-butyl alcohol 0,45 (----) and 0,90 (------) resp.). Values  $\Delta$  are read off from plot (D)<sub>2b</sub> vs. ( $E_T$ )<sub>5</sub> for ( $E_T$ )<sub>6</sub> at solvent composition 0,45 (s. text)

The dependence of the isomerization rate on the composition of the mixture *tert*-butyl alcohol/water (Figs. 4—6) is qualitatively identical to that for the binary solvent propanol/water. The quantitative difference results from different dependences of the preferential sorption on the solvent composition and from the different polarities of propanol and *tert*-butyl alcohol.

Fig. 6. Photochemical *trans* $\rightarrow$ *cis* isomerization of copolymer 3 ( $\bigcirc$ ) and of model compound **2b**( $\bullet$ ) in *tert*-butyl alcohol/water (volume fraction of *tert*-butyl alcohol 0,6). Values  $\triangle$  are read off from plot (D)<sub>2b</sub> vs. ( $E_T$ )<sub>5</sub> for ( $E_T$ )<sub>6</sub> (s. text)



The semiempirical scale of the solvent polarity based on the energy of the charge-transfer band in the visible region of the spectrum of substituted N-alkylpyridinium derivatives, as introduced by Kosower<sup>16</sup>, was applied for evaluating the polymer microenvironment polarity. Monomer (4), whose betain form 2-[4-(3-ethoxy-4-oxidostyryl)pyridinio]ethyl methacrylate (5) shows the solvatochromic intramolecular charge-transfer band, was copoly-

merized with various monomers, 1 included. From the wave number of the absorption maximum which is shifted to a higher wave number with increasing solvent polarity, the polarity of the polymer microenvironment was determined for the copolymer 6 as well as the polarity of the solvent used<sup>17</sup>. The same effects were observed as during the photochemical  $trans \rightarrow cis$  isomerization.



In methanol  $((E_T)_6 = 53,35 \text{ kcal/mol}; (E_T)_5 = 54,39 \text{ kcal/mol})^*)$  as well as in binary solvents the polarity of the copolymer 6 microenvironment was less than the polarity of the solvent used (Figs. 7 and 8). Existence of the effect of the polymer chain on the polarity of its own microenvironment was supported by a shift of the charge-transfer absorption band of copolymers of 4 with 2-vinylpyridine and 4-vinylpyridine (2-VP-4) and (4-VP-4) respectively. The shift of the transition energy,  $E_T$ , of the charge-transfer absorption band of these copolymers to lower values of  $E_T$  as compared to the copolymer

<sup>\*)</sup>  $E_{\rm T}$  = energy of the charge-transfer transition;  $E_{\rm T} = h \cdot v$ ; h, Planck constant; v, frequency;  $E_{\rm T} = 2,859 \, \bar{v} \cdot 10^{-3} \, \text{kcal/mol}$ ; in SI units:  $E_{\rm T} = 11,970 \, \bar{v} \cdot 10^{-3} \, \text{kJ/mol}$ ;  $\bar{v}$ , wave number in cm<sup>-1</sup>.



Fig. 7. Transition energy  $E_T$  of the charge-transfer band, absolute value of  $(\varepsilon_c - \varepsilon_t) \cdot V_i$ and coefficient of preferential sorption  $\gamma$  vs. composition of the solvent mixture propanol/ water; copolymers **6** (**•**) and **3** (O); monomer **5** (**•**) and model compound **2b** ( $\Delta$ ); poly(2-hydroxyethyl methacrylate) ( $\Box$ ). (*u*: volume fraction of propanol; values  $\gamma$  from lit.<sup>15</sup>;  $V_i$ : initial rate of *trans*→*cis* isomerization;  $\varepsilon_c$  and  $\varepsilon_t$  molar absorption coefficients of *cis*- and *trans*-isomers. SI units: 1 kcal/mol=4,1868 kJ/mol)

Fig. 8. Transition energy  $E_{\rm T}$  of the charge-transfer band and absolute value of  $(\varepsilon_{\rm c} - \varepsilon_{\rm t}) \cdot V_{\rm i}$  vs. composition of the solvent mixture *tert*-butyl alcohol/water; copolymers **6** (**•**), **3** (**0**), 2-VP-4 (**v**), and 4-VP-4(**v**), monomer **5** (**•**), and model compounds **2b** ( $\Delta$ ). (v: volume fraction of *tert*-butyl alcohol;  $V_{\rm i}$ ,  $\varepsilon_{\rm c}$  and  $\varepsilon_{\rm t}$  as in Fig. 7. SI units: 1 kcal/mol=4,1868 kJ/mol)

**6** results from a lower polarity of the poly(vinylpyridines) as compared to that of poly(2-hydroxyethyl methacrylate).

When the study of the polymer microenvironment polarity is based on the site of the charge-transfer band, in binary solvents *tert*-butyl alcohol/water and propanol/water, the preferential sorption of *tert*-butyl alcohol and propanol on the polymer coil is manifested by a great difference in the shift of the solvatochromic absorption maximum of the copolymer and model compound. The preferential sorption of water on the polymer coil leads to a reduction of this difference. Only in the case of a high volume fraction of the alcohols in these binary solvents such an increase of the polarity in the microenvironment of the polymer chain is met with that the solvatochromic maximum of the copolymer absorption is shifted to lower wavelengths as compared to the absorption peak of the model compound (s. Fig. 8). The transition energy of the absorption maximum for the charge-transfer solvatochromic band of the model compound **5** and of the copolymer **6** was correlated with an initial value  $|(\varepsilon_c - \varepsilon_l) \cdot V_i|$  of the photochemical *trans* $\rightarrow$ *cis* isomerization of the model compound **2b** and the copolymer **3**. A roughly linear correlation was found (Fig. 9). One can see from Fig. 9 that for individual



Fig. 9. Correlation of transition energy  $E_T$  of the chargetransfer band of **6** and **5** with the absolute value of  $(\varepsilon_c - \varepsilon_t) \cdot V_i$ of **3** and **2b**; copolymer model compound:  $\bigcirc -- \bigcirc$  tertbutyl alcohol/water;  $\bigtriangleup -- \blacktriangle$ propanol/water;  $\bigtriangledown -- \blacktriangledown$  methanol;  $V_i$ ,  $\varepsilon_c$  and  $\varepsilon_t$  as in Fig. 7. (SI units: 1 kcal/mol=4,1868 kJ/mol)

systems the linear correlation between  $E_{T}$  and the initial isomerization rate  $(\varepsilon_c - \varepsilon_t$  is approximately constant for both, the model compound and the copolymer) is very suitable in spite of the existence of a certain scatter. This scatter results on the hand from errors in determining the values to be correlated and, on the other hand, from the fact that the correlated values are based on solvatosensitive processes of different types. In the case of the charge-transfer transition a maximum dipole-dipole interaction solvent-solvatochromic molecule occurs in the basic state and disappears in the excited state<sup>16</sup>; in the course of the *trans* $\rightarrow$  cis photoisomerization of various 4,4'-disubstituted stilbenes a maximum interaction can be observed in the excited state<sup>18,19)</sup>. However, polymer microenvironment polarity does not represent the only factor affecting the rate of the photochemical trans $\rightarrow$  cis isomerization. It is obvious from the correlation of the microenvironment polarity based on the charge-transfer band and the initial  $|(\varepsilon_c - \varepsilon_t) \cdot V_i|$  values for the model compounds 5 and 2b and the copolymers 3 and 6 that at the first stage of the isomerization the linear correlation condition is roughly adhered to. During the following course the relations are becoming more complicated. When we consider that the isomerization of the stilbene units of the copolymer 3 differ from the model compound 2b just in that it occurs only in a medium with different polarity, then kinetic curves expressing the dependence of optical density D on the isomerization time measured for the copolymer 3 and

the model compound **2b** under conditions of the same polarity should be identical. Comparison of these curves obtained either experimentally or by reading off *D* for  $(E_T)_6$  from the optical density yield  $(D)_{2b}$  vs.  $(E_T)_5$  for various times indicates that actually, at the first stage the *trans*-isomer content in the polymer is higher, however, the optical density decreases continuously and after 240min it is lower than the value obtained by correlating  $(D)_{2b}$ with  $(E_T)_5$  so that the content of the *trans*-isomer is lower (Figs. 4—6). Further study is desirable for elucidating these results. In both cases, with copolymer **3** containing stilbene units, and with the copolymer **6** containing a derivative of stilbazol, it was observed that the *trans*-*cis* photoisomerization and the shift of the absorption maximum of the charge-transfer solvatochromic band of the respective copolymers were less sensitive to the solvent polarity as compared to the model compounds **2b** and **5**.

# Conclusion

A non-polar contribution of the polymer chain to the polymer microenvironment polarity was observed. This effect may be estimated from the shift of the charge-transfer absorption band maximum of a copolymer containing a solvatochromic residue in its side chain. This study revealed a further contribution of the polymer chain. After a more rapid initial course of the isomerization the polymeric chain caused a continuous change of the photoisomerization quantum yield  $\Phi_t$ , and the reaction did not achieve its photostationary state during the following time interval and continued at a constant rate. This effect was particularly remarkable in binary solvents with a higher volume fraction of water.

# Experimental Part

# Monomers and model compound

trans-N-4-(4-Nitrostyryl)phenylmethacrylamide (2a):

4-Nitrobenzyl chloride was prepared by nitration of benzyl chloride, adopting a method described for 4-nitrobenzyl cyanide<sup>20</sup>.

mp 70,5—71,5°C (Lit.<sup>21)</sup>: 71°C, lit.<sup>22)</sup>: 70°C).

*trans*-4,4'-Nitrostilbene (*trans*-bis-(4-nitrophenyl)vinylen) was prepared by the reaction of 4-nitrobenzyl chloride with alcoholic sodium hydroxide<sup>24, 25</sup>. The product was recrys-tallized five times from nitrobenzene.

mp 298,5°C (Lit. <sup>23</sup>): 280-285°C, lit. <sup>25</sup>): 296-305°C).

*trans*-4-Amino-4'-nitrostilbene (*trans*-4-aminophenyl-4'-nitrophenylvinylen) was prepared by reducing *trans*-4,4'-dinitrostilbene with sodium polysulfide in ethanol<sup>25)</sup>. The product was crystallized from nitrobenzene. mp 249 °C (Lit.<sup>25)</sup>: 245—245,5 °C).

**2a** was prepared by the reaction of methacryloyl chloride with 4-nitro-4'-aminostilbene in acetone in the presence of triethylamine. The product was recrystallized twice form a mixture ethanol/acetone (1:5, v/v) and three times from dioxane.

C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> (308,3) Calc. C 70,12 H 5,23 N 9,09 Found C 70,33 H 5,22 N 9,02 mp 235,5—237 °C. UV (CH<sub>3</sub>OH)  $\lambda_{max}$  = 370 nm,  $\varepsilon_{\lambda max}$  = 2,91 · 10<sup>4</sup>.

trans-N-4-(4-Nitrostyryl)phenylisobutyramide (2b):

The compound (2b) was prepared by reaction of isobutyric acid chloride (isobutyryl chloride) with 4-nitro-4'-aminostilbene in acetone, in the presence of triethylamine. The amide was crystallized three times from ethanol (with charcoal) and twice from dioxane.  $C_{18}H_{18}N_2O_3$  (310,4) Calc. C 69,65 H 5,85 N 9,03 Found C 69,87 H 5,91 N 9,08

mp 246—248 °C. UV (CH<sub>3</sub>OH)  $\lambda_{max} = 370$  nm,  $\varepsilon_{\lambda_{max}} = 2,78 \cdot 10^4$ .

# 2-Hydroxyethyl methacrylate (1):

1 (ERGON N. P. SPOFA Pharmaceuticals, Prague, Czechoslovakia; at least 99,2% 1, less than 0,3% ethylene dimethacrylate) was used without further purification.

#### Preparation of copolymers

The copolymerizations were carried out in DMF, at a total conc. of comonomers of 0.5 mol/l, with a mole fraction of 0.002 of 2.2'-azoisobutyronitrile as initiator, at  $60^{\circ}$ C, in sealed ampoules. Removal of the air from the polymerization mixture was carried out by the freeze-pump-thaw method. The polymers were precipitated into an excess of anhydrous ether. Unreacted monomer 2 was removed by continual dialyses against DMF and the polymers were dried after their precipitation into ether. Conversion was less than 5%. The method of synthesis, preparation of copolymers of 5 and method of measuring the polarity will be published <sup>17</sup>.

#### Determination of the molecular weight

The viscosimetric measurement was performed at 25°C in an Ubbelohde viscometer. The specific viscosity,  $\eta_{sp}$ , was measured in four solutions whose conc. satisfied the condition  $0.1 < \eta_{sp} < 0.8$ . The copolymer with  $[\eta] = 0.68$  dl/g (in DMF) was isomerized. With respect to a low monomer **2a** content the approximate molecular weight may be calculated<sup>13</sup> to be:  $M_w = 2.45 \cdot 10^5$ .

# Photochemical trans $\rightarrow$ cis isomerization

The photochemical *trans* $\rightarrow$ *cis* isomerization was carried out in glass cells (situated in a thermostat) of a thickness of 9 mm, by using two RVL 125 Tesla mercury discharge lamps and liquid filters characterized by the light transmission from 370 to 550 nm<sup>26</sup>). The absorption values were measured on the SPECORD UV VIS-ZEISS Jena doublebeam spectrophotometer at the wavelength  $\lambda_{max}$  (see Tab. 3). All operations during syntheses, polymerization *etc.* were carried out in the dark.

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