# Characterization and Modeling of Cis−Trans Photoisomerization of a Trifluoromethoxy-Substituted Metacrylate Copolymer Monolayer at a Fluid Interface

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Spread monolayers of a photochromic trifluoromethoxy-substituted metacrylate copolymer were characterized by Π/*A* isotherms under the condition of mainly trans or cis conformation of the photochromic side chains and during the trans restoration process. The isotherms of the individual components, i.e., trans and cis conformation, respectively, and those of variable trans/cis content were described by a new theoretical approach, which takes into account a possible side chain aggregation. A good agreement between the experimental Π/*A* isotherms and the model was achieved for small aggregation numbers and a limited range of surface coverage. The trans/cis content during the trans recovery process was calculated by using the parameters of the individual components. The model correctly reflects the main characteristics of the individual components and the cis−trans transformation process: the minimum area demand per repeating unit of the trans conformation is smaller than that of the cis conformer; the aggregate tendency is higher for the trans conformers at low surface coverage; the trans/cis ratio increases during the trans restoration, where the content depends on the surface pressure.

## Introduction

The approximation of experimental Π/*A* dependencies by an isotherm of insoluble monolayers is a complex task.[1] Usually such approximations are restricted to the case of low surface coverage. The application of such isotherms for mixtures of different components is extremely complicated and often fails in general. The aim of the present paper is to work out and to use a new approach to describe the behavior of mixed insoluble monolayers and to analyze a special case of a polymer monolayer at the air/water interface.

Spread monolayers of a photochromic trifluoromethoxy-substituted metacrylate copolymer (PM(5AzOCF₃-*co*-2OH)) were shown to be able to a light-induced trans−cis isomerization at the air/water interface.[2] The trans−cis photoisomerization in such monolayers may be performed by light irradiation with a xenon source. The trans conformers are preferentially formed in the case of monolayer irradiation at 450 nm; the cis conformers are formed at 360 nm.

Using UV irradiation of 20 mW/cm² intensity, the maximum amount of cis configuration in such monolayers was adjusted within 3 min at different surface coverage. In contrast, the restoration of the trans configuration at 2 mW/cm² intensity was very slow and was nearly completed only within 12 h. Therefore, it was possible to characterize Langmuir films of both isomers almost separately. The main difference in surface chemical behavior of these conformers was obviously caused by a change in minimum molecular area demand per polymer residue. It increases remarkably in the case of cis conformation, which changes the shape of the Π/*A* isotherm and the surface dilation rheological behavior drastically.

The slow recovery of the trans isomer and the comparable short time of Π/*A* isotherm determination presents the possibility to determine isotherms of monolayers with different cis/trans ratio during the conformation recovery. If it would be possible to express the isotherms of the individual components, cis and trans, in an equation which could be generalized, it should be possible to determine the time-dependent cis/trans ratio. For monolayers containing two components, which differ in area demand per molecule, or in the present case in area per polymer residue, the Braun−Le Chatelier principle[3] holds. That means that the cis/trans ratio itself depends on the film pressure and that the content of the component of smaller minimum area demand increases with increasing Π.

Recently, an approach was discussed that allows to describe Π/*A* isotherms containing a phase transition plateau.[4] Taking into account the shape of the Π/*A* isotherm for the cis conformer,[2] this approach seems to be able to express the particularity at least for one single component. A theoretical attempt is developed in the following and then applied to calculate the cis/trans ratio of some experimental Π/*A* isotherms of PM(5AzOCF₃-*co*-2OH) monolayers, which were monitored during the cis to trans recovery.

The prerequisite of such approach is that (1) the polymer monolayer can be treated like a usual one, which contains

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individual molecules; (2) the two conformers behave like two different components of a mixed monolayer, and (3) similar conformers are able to aggregate within the monolayer. The latter prerequisite seems to be useful with regard to the experimental $\Pi/A$ curves, which obviously cannot be described by a more simplified model.

Molecules containing the same hydrophilic groups like the polymer under investigation are known to be orientated in monolayers quite randomly. In the case of the present hydrophobic chains, however, also such molecules are able to form monolayers of a definite order and to aggregate, where the aggregation of similar conformers is favored.

## Experimental Details

The polymer used was a statistical copolymer of (4-trifluoro-methylphenylazo)phenoxypentyl methacrylate and 2-hydroxy-ethyl methacrylate of the formula with $Y = 1 - X$. $X$ was
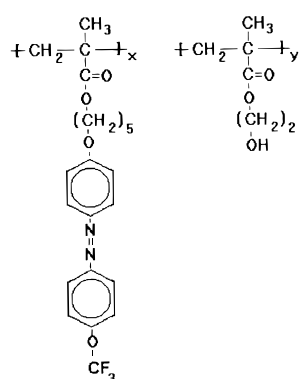


PM(5AzOCF$_3$-*co*-2OH)

analyzed by the F content. The polymer consists of a polymethacrylate with trifluoromethoxyazobenzene units containing side groups as well as 2-hydroxyethyl side groups. The trifluoromethoxyazobenzene-containing monomer was obtained by a multistep synthesis as described earlier.[5] The average molecular mass was 59 000.

The solvents for preparing the spreading solutions ($5.8 \times 10^{-7}$ M/dm$^3$) were chloroform and methanol (10:1) of p.a. grade and purchased from J. T. Baker B. V. (Deventer, Holland). The water used was bidistilled. Further details are given elsewhere.[2]

The monolayers were spread at the surface of a pendant drop. The surface tension of the drop was determined by ADSA (axisymmetric drop shape analysis) and the pendant drop method was used as a microfilm balance,[6] where the monolayer was compressed stepwise by drop volume reduction (further details see ref 2). The drop was kept in an improved measuring cell, which was described in ref 7. During spreading solvent evaporation the air in the cell was substituted by fresh air. The surface pressure $\Pi$ was determined as the surface tension difference between the solvent and the monolayer-covered drop. The spread copolymer was exposed to light only during the measurements.

The trans−cis photoisomerization was realized by light treatment with a xenon source (Müller, Germany) and using colored glass filters with maximum transmission 450 and 360 nm (Schott, Germany) before drop shape analysis. To guarantee reproducible measurement conditions the monolayers were illuminated for 1 h at 450 nm (blue light) to develop the all-trans conformation. In the case of UV irradiation (360 nm) the monolayer molecules are transformed into the cis form. Before

measurements of monolayers in cis form, the monolayers were illuminated for 1 h at 360 nm. Thereafter the monolayers were kept at the usual light exposure of 2 mW/cm$^2$ intensity and after a certain time the $\Pi/A$ isotherms were monitored to characterize the conformation recovery.

## Theory

In refs 8−13 the influence of monolayer aggregation of amphiphilic material on the surface pressure in adsorption or spread monolayers was analyzed. An approach based on the generalized Volmer equation and a quasi-chemical model of aggregation was shown to describe properly the behavior of such systems under equilibrium and dynamic conditions.[14]

We will use this approach for the complex case of surfactant mixtures containing different conformers, which are able to aggregate within the monolayer. First, we will restrict to the situation of relatively small aggregation numbers.

The chemical potentials of components within the surface layer $\mu_i^s$ depend on the composition of the layer and its surface tension $\gamma$. The dependence of $\mu_i^s$ on the composition of real surface layer is given by the well-known Butler's equation[15]

$$\mu_i^s = \mu_i^{os} + RT \ln f_i^s x_i^s - \gamma\omega_i \tag{1}$$

where $\mu_i^{os}$ is the standard chemical potentials that depends on temperature $T$ and pressure $P$. $f_i^s$ are the activity coefficients, $x_i^s$ molecular ratios, and $\omega_i$ the partial molar area of $i$th component or state. Here the superscript "s" refers to the surface (interface).

From Butler's eq 1 follows for the case of a single insoluble surfactant present in the monolayer:

$$d\mu^s = RT\, d(\ln f^s + \ln x^s) - \omega\, d\gamma \tag{2}$$

The Gibb's adsorption equation for a multicomponent system with a chosen Gibb's dividing surface (solvent adsorption equals zero) is

$$d\Pi = \sum_{i=1}^{n} \Gamma_i\, d\mu_i \tag{3}$$

with $\Gamma$ being the adsorption amount for the component or state, $\Pi = \gamma_o - \gamma$ the surface pressure, and $\gamma_o$ the surface tension of the solvent. The superscript on $\mu$ is omitted in eq 3 because this value refers for the case of soluble components to both, the bulk and the surface layer (at equilibrium), and for the case of insoluble components, to surface layer only. Introducing expression 2 into Gibbs' eq 3 and taking into account the dependence of $f^s$ on $x^s$ given by ref 16 leads to

$$\ln f^s = a(1 - \Gamma\omega)^2 \tag{4}$$

and one obtains

$$\frac{d\Pi}{d\Gamma} = \frac{RT}{1 - \Gamma\omega} + 2aRT\Gamma\omega \tag{5}$$

where $a$ is the intermolecular interaction constant.

The approximated integration of eq 5 (with expression $1/(1 - \Gamma\omega)$ being taken out of the integral) yields van der Waals' equation of state for a two-dimensional nonideal gas:

$$\Pi = \frac{RT}{A - \omega} - B = \frac{RT\Gamma}{1 - \Gamma\omega} - B \tag{6}$$

where $A = 1/\Gamma$ is the area per mole in the monolayer, $\omega$ the net

Trifluoromethoxy-Substituted Metacrylate Copolymer

*J. Phys. Chem. B, Vol. 103, No. 18, 1999* **3589**

mole area (partial molar surface area), and $B = aRT\omega/A^2$. Assuming $B = \text{const} = \Pi^*$ (where $\Pi^*$ is cohesion pressure), which corresponds to $f^s = \text{const}$, one can see that eq 6 is just Volmer's equation.[17]

Provided that $f_i^s = \text{const}$ from the Gibbs' and Butler's equations, (3) and (1), respectively, follows for the monolayer formed by $i$ different insoluble components

$$d\Pi = RT\frac{d\sum_i \Gamma_i}{1 - \sum_i \Gamma_i \omega_i} \tag{7}$$

The approximate solution of eq 7 leads to the generalized Volmer equation:[14]

$$\Pi = RT\frac{\sum_i \Gamma_i}{1 - \sum_i \Gamma_i \omega_i} - B_\Sigma \tag{8}$$

with $B_\Sigma$ being the integration constant, which depends on the composition of the monolayer in the case of a multicomponent system.

In the case of aggregation ($n$-mers) of one component, the equation becomes

$$\Pi = RT\frac{\Gamma_1 + \Gamma_n}{1 - \Gamma_1 \omega_1 - n\Gamma_n \omega_1} - B_\Sigma \tag{9}$$

For equilibrium between monomers and aggregates holds[11,12]

$$\Gamma_n = K_n \Gamma_1^n \tag{10}$$

In the case of dimer formation ($n = 2$) from (9) and (10) follows

$$\Pi = RT\frac{\Gamma_1 + \Gamma_1^2 K_2}{1 - \omega_1(\Gamma_1 + 2K_2\Gamma_1^2)} - B_\Sigma \tag{11}$$

In the following it is necessary to change to the determinable total surface for 1 mol of monomers within the monolayer, $A$:

$$A = \frac{1}{\Gamma_\Sigma} = \frac{1}{\Gamma_1 + n\Gamma_n} \tag{12}$$

For dimers this relation corresponds to

$$A = \frac{1}{\Gamma_1 + 2K_2\Gamma_1^2} \tag{13}$$

The combination of (11) and (13) yields

$$\Pi = RT\frac{1 - \Gamma_1^2 K_2 A}{A - \omega_1} - B_\Sigma \tag{14}$$

$\Gamma_1$ will be expressed by $A$ solving the quadratic equation and (13):

$$\Gamma_1 = \frac{-1 \pm [1 + 8K_2/A]^{1/2}}{4K_2} \tag{15}$$

Using the first two terms of progression the quadratic equation may be approximated by

$$\Gamma_1 = \frac{1}{A}\left(1 - \frac{K_2}{4A}\right) \tag{16}$$

The constant value $K_2$ has the dimension of surface per mole. Therefore, it can be favorably substituted by the critical surface molarity of dimerization within the monolayer $A_c$, i.e., $K_2 = A_c$. Inserting (16) into (14) one obtains

$$\Pi = RT\frac{1 - (A_c/A)(1 - A_c/4A)^2}{A - \omega_1} - B_\Sigma \tag{17}$$

It can be seen that (17) can be applied when $A_c < A$. In the case $A_c \ll A$ a good approach for (16) is $\Gamma_1 = 1/A$. Therefore (17) simplifies to

$$\Pi = RT\frac{1 - (A_c/A)}{A - \omega_1} - B_\Sigma \tag{18}$$

For $A_c = 0$, eqs 17 and 18 transform into the Volmer eq 6. For aggregates and $n > 2$ a general solution is

$$\Pi = RT\frac{1 - (n - 1)\Gamma_1^n K_2 A}{A - \omega_1} - B_\Sigma \tag{19}$$

with $\Gamma_1$ being the root of an equation with the exponent $n$

$$A = \frac{1}{\Gamma_1 + (n - 1)K_n\Gamma_1^n} \tag{20}$$

Unfortunately, the exact solution of (20) for $n = 3$ and 4 becomes very complex and for cases $n > 4$ a solution cannot be found. Nevertheless, $\Gamma_1 = 1/A$ is a good approach for $A_c \ll A$ and all values of $n$, provided the aggregation number is not too large.

For uniformity we will apply for $K_n$ the critical molar surface of aggregation $A_c$ as $A_c^{n-1} = K_n$. Therefore, from (19) the following equation is found, i.e., the equation of state for a monolayer containing aggregates of not very large aggregation numbers

$$\Pi = RT\frac{1 - (n - 1)(A_c/A)_{n-1}}{A - \omega_1} - B_\Sigma \tag{21}$$

Obviously, eqs 17, 18, and 21 yield a more moderate slope of the isotherm in comparison to Volmer's isotherm (6) for aggregation in insoluble monolayers and small values of $A$.

In following the situation in the absence of monomer will be analyzed; i.e., the whole monolayer contains aggregates only. Considering eq 9, we get

$$\Pi = RT\frac{\Gamma_n}{1 - n\Gamma_n \omega_1} - B_\Sigma \tag{22}$$

Taking into account (12) for the present case

$$A = \frac{1}{\Gamma_\Sigma} = \frac{1}{n\Gamma_n} \tag{23}$$

thus leading to

$$\Pi = \frac{RT}{n(A - \omega_1)} - B_\Sigma \tag{24}$$

Obviously, in this case the isotherm yield smaller values of $\Pi$ in the whole range of $A$ in comparison to Volmer's isotherm (6).

In the case of a mixed monolayer consisting of two components 1 and 2, which may aggregate and form $n$- and $m$-mers, the generalized Volmer eq 8 becomes

$$\Pi = RT\frac{\Gamma_1 + \Gamma_2 + \Gamma_n + \Gamma_m}{1 - \omega_1(\Gamma_1 + n\Gamma_n) - \omega_2(\Gamma_2 + m\Gamma_m)} - B_\Sigma \quad (25)$$

We have to substitute, however, all $\Gamma$ values by area per mole, i.e., a value that really can be determined.

$$A = \frac{1}{\Gamma_\Sigma} = \frac{1}{\Gamma_1 + \Gamma_2 + \Gamma_n + \Gamma_m} \quad (26)$$

This leads to the ratio of total adsorption of the components, i.e., adsorption regarding to monomers or their mass $\alpha$

$$\alpha = \frac{\Gamma_1 + n\Gamma_n}{\Gamma_2 + m\Gamma_m} \quad (27)$$

Unfortunately, in the case of monomers and aggregates presented simultaneously for one monolayer component, it is impossible to give a solution of (25), which contains only $A$, $\alpha$, and $\omega_i$. Nevertheless, in the presence of only monomers or only aggregates of one component, a simpler relation results for a mixed monolayer.

1. The monolayer consists monomers of 1 and 2 only ($\alpha = \Gamma_1/\Gamma_2$):

$$\Pi = \frac{RT}{A - \omega_1 - (\omega_2 - \omega_1)/(1 + \alpha)} - B_\Sigma \quad (28)$$

2. In the monolayer are monomers of 1 and $m$-mers of 2, ($\alpha = \Gamma_1/m\Gamma_m$)

$$\Pi = \frac{RT}{m}\frac{(1 + \alpha m)/(1 + \alpha)}{A - \omega_1 - (\omega_2 - \omega_1)/(1 + \alpha)} - B_\Sigma \quad (29)$$

3. The general case, with $n$-mers of 1 and $m$-mers of 2 within the monolayer, ($\alpha = n\Gamma_n/m\Gamma_m$)

$$\Pi = \frac{RT}{m}\frac{(1 + \alpha m/n)/(1 + \alpha)}{A - \omega_1 - (\omega_2 - \omega_1)/(1 + \alpha)} - B_\Sigma \quad (30)$$

Obviously, (28) and (29) are special cases of eq 30 for $n = m = 1$. In the cases $\alpha = 0$ or $a = \infty$, i.e., when only one component or state is present, from (30) results (24) for the states 2 or 1, respectively:

$$\Pi = \frac{RT}{n(A - \omega_1)} - B_{\Sigma 1} \qquad \Pi = \frac{RT}{m(A - \omega_2)} - B_{\Sigma 2} \quad (31)$$

These equations transform into the Volmer isotherm (6) for the case $n = m$. The constant values $B_{\Sigma i}$ in eq 31 are usually different. Therefore, it is necessary to determine $B_\Sigma$ in (28)−(30) by using an average value normalized to the adsorption. The general form for monomers or aggregates is

$$B_\Sigma = \frac{B_{\Sigma 1}n\Gamma_n + B_{\Sigma 2}m\Gamma_m}{n\Gamma_n + m\Gamma_m} = \frac{\alpha B_{\Sigma 1} + B_{\Sigma 2}}{1 + \alpha} \quad (32)$$

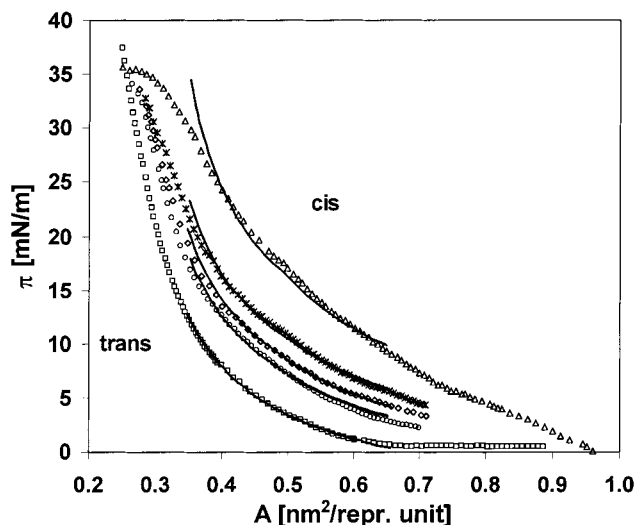Obviously, the only additional parameter for the mixture is $\alpha$ as it is in the eqs 28−30.



**Figure 1.** Experimental $\Pi/A$ dependencies of PM(5AzOCF$_3$-*co*-2OH); ($\square$) photochromic side chains mainly in trans conformation; ($\triangle$) after UV irradiation, photochromic side chains mainly in cis conformation; ($*$) 3, ($\diamondsuit$) 6, and ($\bigcirc$) 9 h after stopping the UV irradiation. Solid lines were fitted by using eq 31 for $\square$ and $\triangle$, and (33) for $*$, $\diamondsuit$, and $\bigcirc$.

Therefore, eq 30 may be written as

$$\Pi = \frac{RT}{m}\frac{(1 + \alpha m/n)/(1 + \alpha)}{A - \omega_1 - (\omega_2 - \omega_1)/(1 + \alpha)} - \frac{\alpha B_{\Sigma 1} + B_{\Sigma 2}}{1 + \alpha} \quad (33)$$

where all constants are related to the individual components, but the parameter $\alpha$ yields the ratio of mass of the components, or conformers within the monolayer.

Actually $\alpha$ depends on the surface pressure. From the Butler equation 1 and taking into account eq 27

$$\alpha = \alpha_0\exp\left(\frac{\Pi(\omega_2 - \omega_1)}{RT}\right) \quad (34)$$

with $\alpha_0$ being the ratio at the zero surface pressure. Equation 34 is a generalization of the Joos equation[18] for the case of conformer aggregation. Therefore, $\alpha$ may increase with increasing surface pressure when $\omega_1 > \omega_2$.

**Experimental Results and Discussion**

Figure 1 shows the $\Pi/A$ isotherms determined for the individual components, i.e., the monolayers in trans and cis conformation. After monitoring the curve in cis conformation, the monolayer was expanded, and every 3 h a new $\Pi/A$ isotherm was determined.

The curves for the individual components are in good agreement with those reported in ref 2. The experiments were repeated and the deviations between the experimental curves were negligible. The curves during conformation recovery are shifted to lower surface pressure in comparison to this of cis conformation. The $\Pi$ values at definite surface coverage, however, are slightly higher than those found in recovery experiments at a definite starting surface coverage shown in Figure 3 of ref 2. This is not surprising, when taking into account the different experimental conditions. The $\Pi/t$ dependencies shown in Figure 3 of ref 2, where taken at a constant drop volume, i.e., the monolayers were constantly in a compressed state, with a $\Pi$ decay resulting from conformation recovery. In contrast, in the case of the experiments reported here the

Trifluoromethoxy-Substituted Metacrylate Copolymer

*J. Phys. Chem. B, Vol. 103, No. 18, 1999* **3591**

**TABLE 1: Parameter Calculated by Fitting the Curves of Mainly Trans and Cis Conformers and Using Eqs 31**

| trans | | cis | |
|---|---|---|---|
| $A = 0.5-0.65$ nm$^2$/repeating unit | | | |
| $\omega_1$ | 0.2 | $\omega_2$ | 0.26 |
| $B_{\Sigma 1}$ | 5.606 | $B_{\Sigma 2}$ | 0.488 |
| $n$ | 1.484 | $m$ | 1.001 |
| $A = 0.35-0.5$ nm$^2$/repeating unit | | | |
| $\omega_1$ | 0.2 | $\omega_2$ | 0.26 |
| $B_{\Sigma 1}$ | 5.558 | $B_{\Sigma 2}$ | −5.141 |
| $n$ | 1.499 | m | 1.5 |

**TABLE 2: Parameter $\alpha$ Calculated for Fixed Parameters of Table 1 and by Fitting Eq 33**

| time after UV illumination (h) | $\alpha$ | |
|---|---|---|
| | $A = 0.35-0.5^a$ | $A = 0.5-0.65^a$ |
| 3 | 0.8 | 0.7 |
| 6 | 1.45 | 1.40 |
| 9 | 2.25 | 2.15 |

[a] In nm$^2$/repeating unit.

monolayers were expanded after every $\Pi/A$ monitoring. When taking into account, that the cis/trans equilibrium is a function of the film pressure, the lower $\Pi$ values of the $\Pi/t$ dependencies in Figure 3 of ref 2 at comparable surface coverage become understandable.

First, the curves of the individual components, cis and trans, respectively, were analyzed. By fitting eqs 31 to these curves, it became clear that there is no possibility for fitting the whole range of surface coverage with only one parameter set. This, however, is usually the case when $\Pi/A$ dependencies of monolayers are fitted by theoretical isotherms. Therefore, two ranges of surface coverage were selected for fitting, 0.35−0.5 nm$^2$/repeating unit and 0.5−0.65 nm$^2$/repeating unit. The results are given in Table 1.

The resulting curves are shown as solid lines in Figure 1. The approximation is quite good with the exception of the curve for the cis conformer at higher surface coverage. The approximation for the two ranges of surface coverage leads the cis conformer to a curve with a kink point. Actually, such shape of curve is often found. It is explained by phase transition, which is physically consistent with the model presented, i.e., a change of the aggregation number. It is also found, however, that often this phase transition region is not clearly pronounced, thus leading to curves with ranges of different slopes which are not clearly separated. Obviously this is the case for the curve of the cis conformer.

At higher surface coverage, however, the fitting strongly fails. On the one hand, this may be caused by an increasing aggregation. On the other hand, such a decrease of $\Pi/A$ slope often is caused by an onset of monolayer collapse. It should be noticed, however, that no hysteresis between $\Pi/A$ curves for monolayer compression and expansion was found (see Figure 1 of ref 2). For nonpolymer monolayers this would be a strong hint to exclude monolayer collapse. Such interpretation is also supported by the surface rheological dilation behavior. In fact, however, such conclusion of analogy to monomolecular monolayers may be misleading. The hysteresis may not be characteristic for polymer monolayer collapse, because polymer monolayers have much more possibilities of rearrangement in comparison to monomolecular layers, which also may lead to a decrease of area demand per repeating unit.

Furthermore, it has to be taken into account that we were not using the more strict eq 21, but the simplified version eq 31. This also may explain the large differences between the calculated and the experimental curves of the cis conformer.

The parameter $B_{\Sigma 2}$ of the cis conformer becomes negative for the range 0.35−0.5 nm$^2$/repeating unit. $B_{\Sigma}$ takes into account the whole interaction between the monomers within the monolayer, and therefore it may be also negative.

In contrast to the isotherm of the cis conformer the results show that the curves of trans conformation may be well fitted nearly by the same parameters in the whole range 0.35−0.65 nm$^2$/repeating unit. It is noteworthy that the aggregation number

$n > 1$ even for the range 0.5−0.65 nm$^2$/repeating unit. It can be interpreted as a high tendency to aggregate for the trans forms.

For the calculation we took care to optimize $\omega_1$ and $\omega_2$ that these values were equal in the whole range 0.35−0.65 nm$^2$/repeating unit, as they correspond to the area demand of monomers. Differences between the area demand of monomers and aggregates were not considered in the theory presented.

Knowing the parameters $n$, $\omega_1$, $B_{\Sigma 1}$, and $m$; $\omega_2$, $B_{\Sigma 2}$, the parameter $\alpha$ was fitted for the two ranges 0.35−0.5 and 0.5−0.65 nm$^2$/repeating unit. The values are given in Table 2; the resulting curves are shown as solid lines in Figure 1. As the parameters $n$ and $m$ are of the same order the relation between trans and cis conformers in the monolayer $\Gamma_1 \approx \alpha\Gamma_2$, with 1 standing for trans and 2 for cis.

Although only one parameter was varied, the results show a good agreement between the experimental and calculated curves, with the exception of the range of high surface coverage, i.e., >0.4 nm$^2$/repeating unit. After stopping the UV irradiation, $\alpha$ increases with time; i.e., the content of trans conformation in the monolayer increases. This result is trivial, but it is correctly reflected by the model.

Also the dependence of $\alpha$ from $\Pi$ is correctly expressed by the results. The content of the component with lower area demand per unit increases with increasing $\Pi$, which is in agreement with the Braun−Le Chatelier principle.

## Conclusion

$\Pi/A$ isotherms of a photochromic trifluoromethoxy-substituted methacrylate copolymer were monitored after light exposure at 450 nm and UV irradiation at 360 nm, and thus guarantee a mainly trans and cis conformation of the photochromic polymer side chains, respectively. After stopping the UV irradiation the trans conformation is slowly restored. During the conformation recovery, $\Pi/A$ dependencies were determined, which contain side chains with increasing content of trans conformation.

Under the prerequisite that such monolayers can be treated as consisting of monomers, a new theoretical approach was used to describe the $\Pi/A$ isotherms and to evaluate the content of cis and trans conformers during the recovery process. The model is based on a type of the Volmer isotherm and takes into account the possible aggregation of monolayer monomers. In a definite range of surface coverage and for small aggregation numbers, a good agreement was achieved between the model and the experimental $\Pi/A$ curves of the individual components, i.e., side chains in cis and trans conformation. Only a three-parameter set was necessary to characterize these components. The model uses a constant area demand per monomer over the whole range of description, i.e., 0.35−0.65 nm$^2$/repeating unit, and variable aggregation number and a parameter accounting for the interaction. The minimum area demand of the trans form calculated by best fitting was smaller than that of the cis form. The tendency for trans conformers to aggregate is obviously higher in comparison to that of the cis conformers at low surface

coverage. These results are expected and correctly expressed by the model.

Applying the parameter sets of the individual components, the conformation changes during the trans restoration was characterized by using only one additional parameter. This parameter allows estimating the actual ratio between cis and trans conformers within the monolayer. The model also correctly predicts the main characteristics for the mixtures: the monolayer content of trans conformers increases during the restoration process, and it increases too with rising surface pressure. This is in agreement with the differences of the minimum area demand of the cis and trans conformers and confirms the tendency of cis to trans transformation under external pressure.

Therefore, it can be concluded that the model presented is proved to predict correctly the behavior of a mixed monolayer. The mixing ratio of the monolayer components can be calculated when the parameters of the adsorption isotherms of the individual components are known. Furthermore, the prerequisites chosen to describe the polymer monolayers were shown to lead to meaningful results. That means the polymer monolayer can be described by treating it like a usual monolayer, consisting of side chain type molecules, which are not polymerized. The assumption of side chains aggregation in polymer layers is suited to describe the monolayer behavior of such systems. The two conformers, cis and trans conformers, respectively, behave like two different components of a mixed monolayer.

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