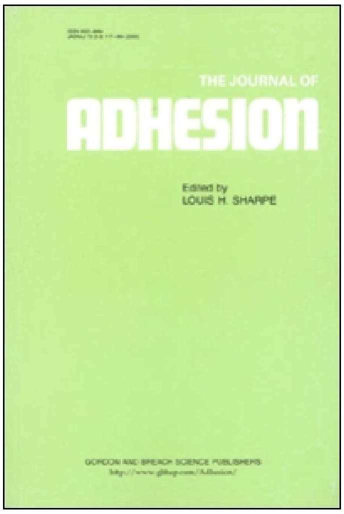

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Infrared Reflection Spectroscopy of Polycyanurate Thin Films on Solids-State of the Interphase

Wulff Possart[a]; Detlef Fanter[a]; Monika Bauer[a]; Andreas Hartwig[b]; Otto-Diedrich Hennemann[b]
[a] Fraunhofer-Institut für Angewandte Materialforschung, Außenstelle Teltow, tow, Germany [b] Fraunhofer-Institut für Angewandte Materialforschung, Bremen, Germany

To cite this Article Possart, Wulff , Fanter, Detlef , Bauer, Monika , Hartwig, Andreas and Hennemann, Otto-Diedrich(1995) 'Infrared Reflection Spectroscopy of Polycyanurate Thin Films on Solids-State of the Interphase', The Journal of Adhesion, 54: 1, 261 — 275

To link to this Article: DOI: 10.1080/00218469508014394

URL: http://dx.doi.org/10.1080/00218469508014394

J. Adhesion, 1995, Vol. 54, pp. 261–275
Reprints available directly from the publisher
Photocopying permitted by license only

Infrared Reflection Spectroscopy of Polycyanurate Thin Films on Solids – State of the Interphase*

WULFF POSSART, DETLEF FANTER, MONIKA BAUER

Fraunhofer-Institut für Angewandte Materialforschung, Außenstelle Teltow,
Kantstraße 55, D-14513 Teltow, Germany

ANDREAS HARTWIG, OTTO-DIEDRICH HENNEMANN

Fraunhofer-Institut für Angewandte Materialforschung, Neuer Steindamm 2,
D-28719 Bremen, Germany

(Received June 1, 1994; in final form December 12, 1994)

FTIR reflection spectroscopy was used to characterize thin films of a cyanurate prepolymer on evaporated aluminium and on silicon single crystal wafers. Both substrates are covered by their native oxides. The optical function of the prepolymer is derived from ATR measurements. The measured thin film reflectance spectra have to be interpreted in comparison with the corresponding bulk spectra obtained by simulation. All samples re-produce the bulk composition. The cyanate groups of the prepolymer are not involved in specific intermolecular interactions or in preferential orientation. This is also found for the triazine rings on Si. On Al, however, a considerable excess of triazine rings are oriented parallel to the interface. The vibration frequencies of the triazine groupings that are perpendicular to the Al substrate show a red shift to some 2–8 cm^{-1}. This special interaction effect does not occur on Si. Both the preferential orientation and the specific inter-molecular interaction act at least 100 nm into the prepolymer layer.

KEY WORDS Infrared reflectance spectroscopy; cyanurate prepolymer; aluminium or silicon substrate; thin films; molecular orientation; molecular interaction.

1. INTRODUCTION

The infrared reflectance method is able to provide information on the structure of an organic layer without the use of probe molecules and with comparably good spectral sensitivity. As a nondestructive measurement it can be applied in various environments from laboratory atmosphere to ultra high vacuum conditions. Therefore, it is not surprising that a huge number of infrared reflection studies have appeared which cover polymer surfaces,[1] molecular adsorption at solids,[2–4] monolayers[5,6] the state of thin films,[7] etc. Only a small selection of references can be cited here. Detailed conformational and orientation information concerning the nature of the film can be derived, presuming that correct assignment of the vibration modes as well as their transition

---

* One of a Collection of papers honoring James P. Wightman, who received the 13th Adhesive and Sealant Council Award at the ASC's 1993 Fall Convention in St. Louis, Missouri, USA, in October 1993.

dipole moments is available. Within this frame, the method is equally well used for studying intermolecular bonding, phase transitions and interphase composition. That potential is especially interesting in conjunction with the adhesive properties of polymer coatings on solids, *e.g.* Refs. 2, 8–12. In this paper, we report the results of the first infrared reflectance study on thin layers of a cyanurate prepolymer on aluminium and on silicon. Polycyanurates form polymer networks[13] that combine high thermal stability with low dielectric loss and good chemical resistance. Processing is easy in the prepolymer state and the resins show good adhesive strength at elevated temperatures. The infrared characterization of the physical state of cyanurate films improves the understanding of the adhesion properties.

2. MATERIAL CHARACTERIZATION, SAMPLE PREPARATION, AND EXPERIMENT

For this study, a prepolymer was synthesized by thermal cyclotrimerization of dicyanato bisphenol A (DCBA). Figure 1 depicts the chemical formulae for the monomer, for the cyclotrimer as the result of the first curing step, and a cut-out of a larger network piece. The reactivity of the cyanate groups (OCN) does not depend on the molecule's dimension. The curing reaction is highly selective and provides a uniform chemical structure throughout the network.[13] The triazine rings form the knots of the network. For our purposes, the curing reaction was terminated at 45 mole% conversion of cyanate groups, thus providing an easily-soluble prepolymer. Applying HPLC and the theory of gelation,[13,14] the number distribution is obtained for the oligomer molecules. It consists of 75.6% monomer, 12.5% trimer, 4.6% pentamer, and 2.3% heptamer. The remaining 5% contains all larger molecules.

Customary silicon single crystal wafers and aluminium layers are used as solid substrates. The Al layers are produced by electron beam evaporation in an oil-free vacuum. Both substrates were stored and coated at the laboratory atmosphere.

The wafers are extremely flat (root mean square roughness RMS 0.2 nm in AFM pictures). They are covered by a native oxide layer of uniform lateral thickness (about 1 nm by AES and ellipsometry). XPS reveals a nonstoichiometric composition for it. On top of that layer, some 0.5 nm of a uniform carbonaceous contamination of the hydrocarbon type is found (XPS).

The surface of the evaporated Al layers (in oil-free vacuum) possesses a much greater roughness of RMS 4–10 nm (AFM). The uniform nonstoichiometric oxide layer (*ca.* 2.8 nm thick) contains some 70% of oxygen bound in hydroxidic states. The remaining oxygen forms an oxide that is roughly estimated as $Al_{0.66}O_{0.34}$. Again, a contamination is spread uniformly but it contains not only aliphatic carbon. A certain amount is bound to oxygen.

Thin layers are prepared by spin coating or by dip coating from a prepolymer solution in 1,1,1-trichloroethane. Variation of the concentration provides a thickness range from about 2 nm to some 100 nm. Ellipsometry shows laterally uniform layers. Within the sensitivity of XPS, AES and infrared spectroscopy, no residual solvent is detected in the dry films.

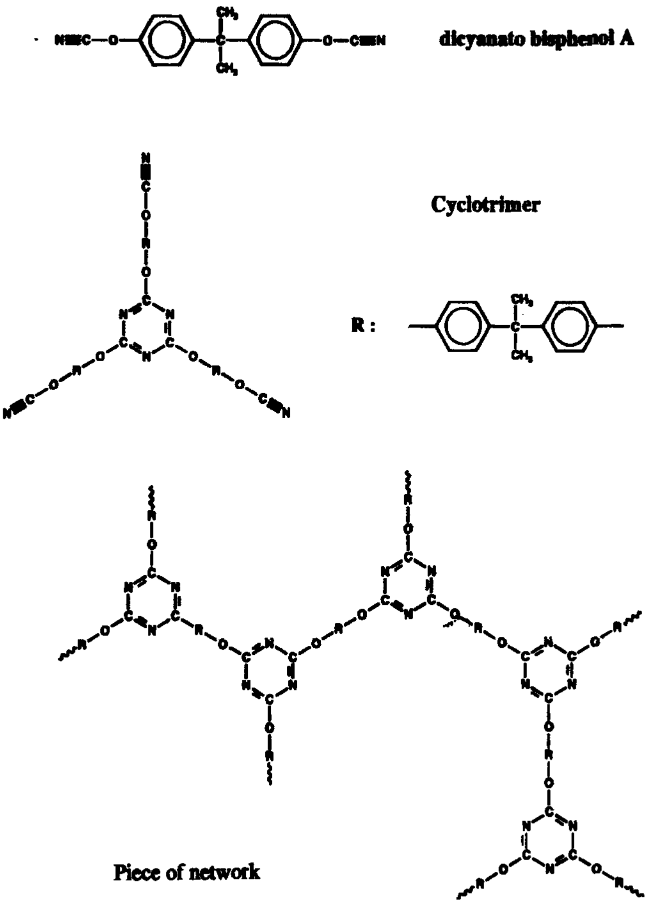

FIGURE 1 Chemical formulae of dicyanato bisphenol A (DCBA), of the cyclotrimer, and of a larger piece of the network.

The infrared reflection spectra of the spin-coated samples are obtained with an FTS 60B (Bio-Rad) equipped with an MCT detector, a reflection accessory SEAGULL (Harrick) and a KRS-5 wire grid polarizer. A FTIR spectrometer Model 740 (Nicolet) with MCT detector, a reflection accessory Model 500 (Spectratec) and KRS-5 wire grid polarizer served for the investigation of the dip-coated samples. The two spectrometers were used for convenient organization of the measurements on different series of samples. In any case, particular care has to be taken to reduce the noise and to avoid base line distortions. An optimum is achieved with an immediate coupling of layer preparation and infrared spectroscopy. Therefore, the investigation consists of the following steps:

Oxide thickness measurement on the bare substrate by ellipsometry.
Infrared reflection spectrum at the bare substrate as the background spectrum.

- # Preparation of prepolymer layer.
- # Infrared reflection spectrum for the complete specimen as the sample spectrum.
- # Ellipsometric thickness determination for the prepolymer coating.
- # Calculation of the reflectance spectrum as the quotient of sample and background spectra.

Good quality reflectance spectra are obtained on aluminium with *p*-polarized light at 80° incidence for prepolymer layers of ≥ 3 nm thickness. Figure 2 gives an example. On Si, at least some 7 nm of prepolymer are needed under optimized conditions (*s*-polarized light, angle of incidence $\Theta_e = 50°$) to achieve similar quality.

3. SPECTROSCOPIC RESULTS

3.1. DCBA Prepolymer in Bulk

For more than 20 years infrared spectroscopy has been applied for substance identification and for the determination of the degree of cyanate conversion in the literature (see review, Ref. 13). Unfortunately, none of the sources provides a detailed normal coordinate analysis for the absorption bands in the mid infrared. Figure 3 depicts a transmission spectrum of a prepolymer layer on a KBr plate and a band assignment that rests upon the local mode concept. The assignment is done with the software IR-MENTOR (Bio-Rad, Sadtler Div.) and checked with the help of various catalogues.[15–17] The typical vibrations of the cyanate group of the triazine ring are

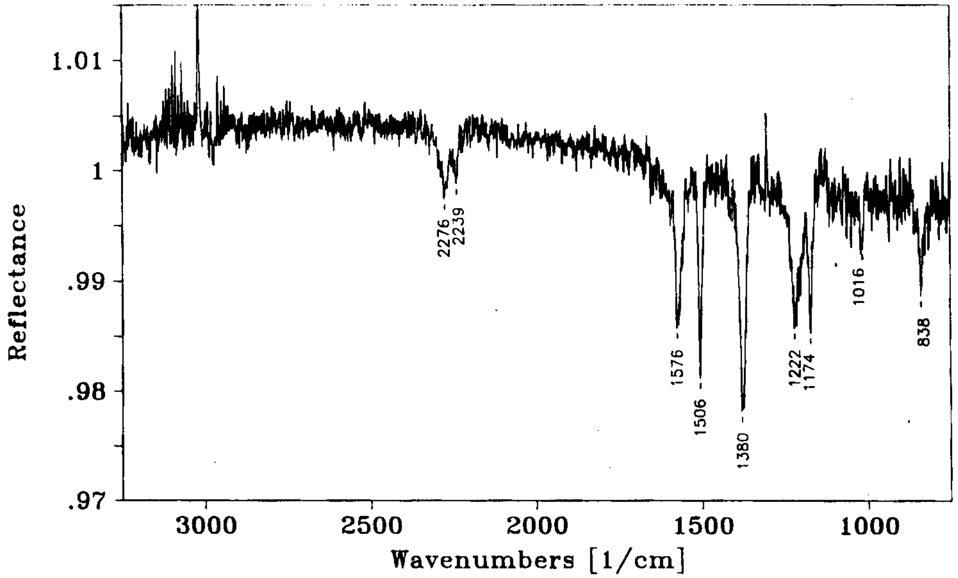

FIGURE 2 Reflectance spectrum (raw data) obtained from a 5.6 nm layer of prepolymer spun on Al. Spectral resolution 2 cm^{-1}, angle of incidence $\Theta_e = 80°$, *p*-polarization.

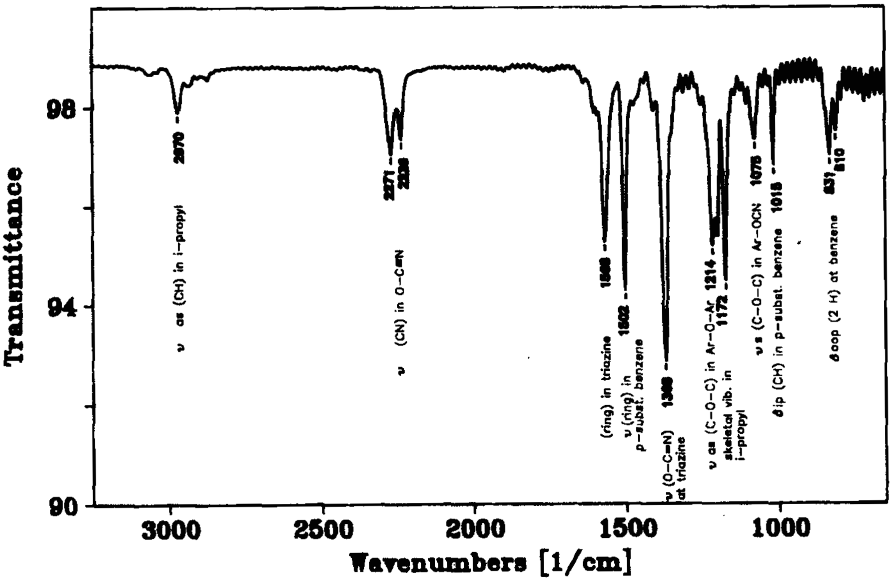

FIGURE 3 Transmittance spectrum (raw data) obtained from a prepolymer layer on KBr. Band assignment due to the literature.[15–21] Spectral resolution 2 cm^{-1}, unpolarized light, normal incidence.

identified according to the literature.[18–21] We note the limited precision of such an assignment. That might confine the discussion of spectral peculiarities in terms of changes of morphology or bond state of organic molecules in interphases or thin films.

In addition, the interpretation of thin film reflectance spectra requires the optical function of the prepolymer in the bulk state

$$n_P^*(\tilde{\nu}) = n_P(\tilde{\nu}) - i \cdot k_P(\tilde{\nu})$$

n_P = refractive index

k_P = extinction coefficient

This material function is derived from a number of ATR spectra obtained for thick prepolymer coatings on a germanium crystal. Due to the conditions of measurement, the evanescent wave penetrates some 0.17 to 0.9 μm into the prepolymer. The spectra monitor the bulk properties, therefore. The software FSOS[22] is used for calculating the corresponding optical function for each spectrum. The repeated determination proves that the band position in the k_p-spectrum can be reproduced with better than 0.5 cm^{-1} accuracy. Only for noisy regions, a slightly increased scatter of (1 cm^{-1}) is found. Hence, the exactness of the band positions is ruled mainly by the spectral resolution of 2 cm^{-1} chosen in the measurements.

The determination of peak heights refers to linear baselines that are defined for suitable spectral regions. The absolute values of peak height differ considerably for the various k_p-spectra although the base line set is always the same. the situration is improved by choosing an infrared band as internal reference. The band at 1015 cm^{-1} is considered as suitable because the in-plane bending vibration of the CH-groups in the benzene rings (compare Fig. 3 for assignment) would certainly not interact with the substrate. Moreover, the vibration appears so frequently in the prepolymer that some preferential molecular orientation should not change the intensity of that band remarkably. With this reference, the relative peak heights are reproduced with a standard deviation of (2–3)% for well separated bands. Even for strongly overlapping bands the error reaches (8–10)% only on occasion. As a further test, the ATR spectra are recalculated from the optical functions with the FSOS software. The simulated spectra correspond fully to the measurements. Only the absolute peak heights are systematically underestimated by (2–5)%. It is inferred from these tests that the calculated optical function has sufficient quality for spectra simulation. The software FSOS produces no substantial numerical errors.

3.2. Prepolymer Layers on Al and Si

Infrared absorption bands of a thin film reflection spectrum may differ from the bands in a transmission spectrum with respect to frequency position and band intensity. This is due to anomalous dispersion caused by a strong variation of the refractive index, n_p, at any absorption frequency.[7] Those effects depend also on the angle of incidence, Θ_e, and on the absorption strength. Therefore, it is dangerous to draw conclusions about intermolecular bonding or about preferential molecular orientation immediately from the reflectance spectra as depicted in Figure 2. The artifactual spectral distortions must be appreciated before band shifts or intensity changes may be interpreted in terms of changes in prepolymer properties. We do that in the following way.

The background spectrum is simulated at the given measuring conditions (Θ_e and polarization direction) for the bare substrate as a semi-infinite solid covered by an isotropic oxide layer of uniform thickness in air. This is again done with FSOS package. The optical functions of air, substrate (Al or Si) and oxide are taken from the literature.[22–26] The actual oxide thickness is determined by ellipsometry. For the sample spectrum, the prepolymer's optical function of the bulk state is added as it comes out of the ATR investigation. Ellipsometry provides the prepolymer thickness. The simulation uses these data to calculate the sample spectrum for a system of two uniform isotropic layers made of prepolymer and oxide on the semi-infinite substrate in air. The quotient of sample and background spectra yields the reflectance spectrum as it would be measured for the specimen if the prepolymer layer would possess exactly the bulk properties. Hence that simulated reflectance spectrum provides the right reference for the discussion of peculiar thin film features. Figure 4 compares such a simulated bulk-like spectrum with the actually measured thin-film spectrum for a given thickness, d_p, on the Al substrate.

Since the geometric parameters are the same for each pair of simulation and spectroscopic measurement, comparison between the measured infrared spectrum and the corresponding simulation result provides exclusively all derivations in the optical function of the real thin film sample with respect to the bulk. We can reasonably expect that the substrate material does not "feel" the presence of the prepolymer through the oxide layer. Thus, all observed derviations are due to changes in the prepolymer and/or in the oxide. We note that the following peculiarity has to be kept in mind in this

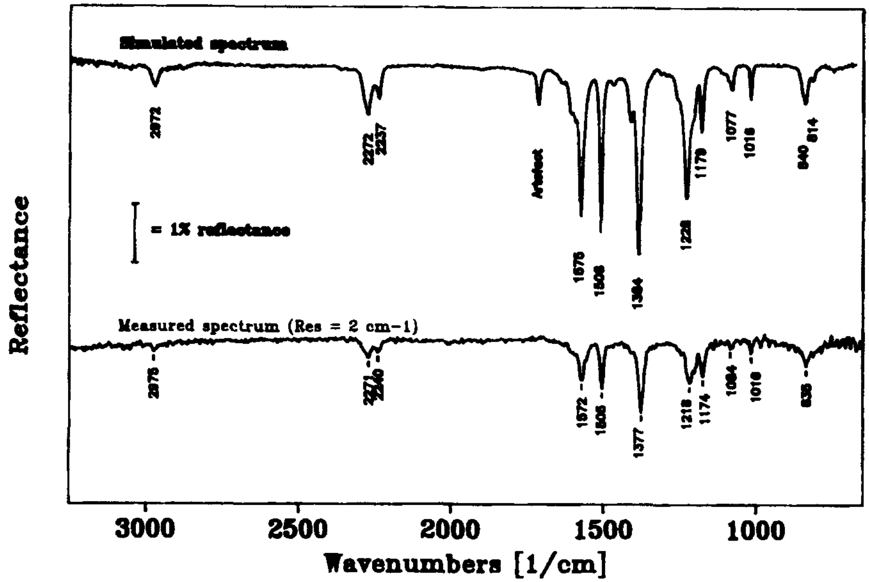

FIGURE 4 Simulated and measured reflectance spectra for 7.4 nm prepolymer on Al after spin coating. $\Theta_e = 80°$, p-polarized light.

context. The succeeding conclusions refer to different sets of prepolymer molecules on Al and Si, respectively. Due to the surface selection rule on Al, only those vibrations contribute to an infrared absorption band that have a significant component of their transition dipole moment in a perpendicular direction to the substrate surface. On Si, *s*-polarized light has to be used in order to obtain sufficient spectral sensitivity. Hence, the complementary set of orientations is detected here. Only transition dipoles with a significant component perpendicular to the plane of incidence are able to absorb energy from the light.

What deviations are observed? To start with the frequency position of the main stretching vibrations, we find some frequency reductions in the measured spectra as referred to the prepolymer's bulk behavior while other bands retain their position.

For example, the positions of the valence vibrations attributed to the cyanate group and the neighboring carbon atom in the benzene ring do not change with prepolymer thickness either on Al or on Si. Figure 5 gives the (CN) stretching mode as an example. Within the expected error, that is true for both substrates.

The skeletal vibration of the i-propyl group between the benzene rings shows bulk behavior on Si as well, see Figure 6. On the aluminium substrate, however, this vibration has a reduced frequency with respect to the bulk.

The valence vibrations of the triazine ring and its surroundings shift on Al unambiguously to lower frequencies. The strongest shift with some 8 cm^{-1} is observed for the oxygen bridge from the triazine to the benzene ring, see Figure 7.

Similarly, the frequency of $\nu(-\mathrm{N{=}C{-}O})$ is reduced by about 6 cm^{-1} and $\nu(-\mathrm{N{=}C}-)$ of the triazine ring itself loses more than 2 cm^{-1}. The benzene ring vibration at *ca.* 1505 cm^{-1} is also slightly involved with some 2 cm^{-1} reduction, see Figure 8.

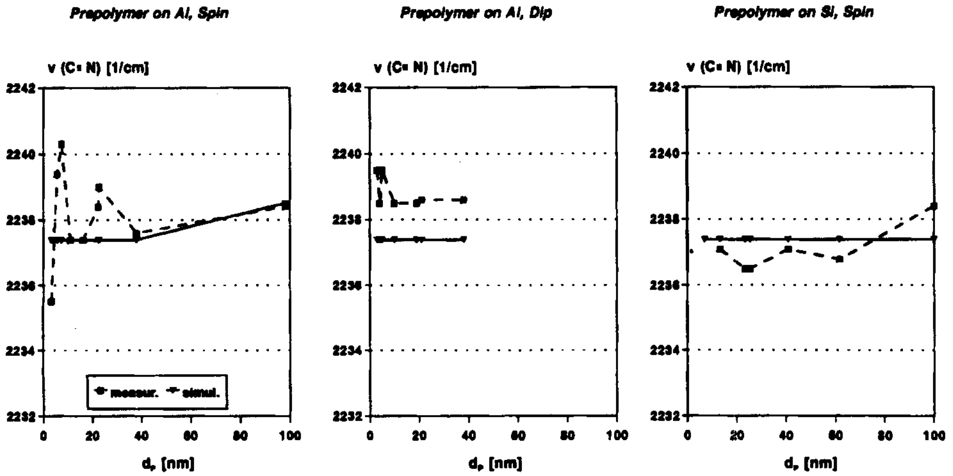

FIGURE 5 Simulated and measured positions of the stretching mode $\nu(C \equiv N)$ *versus* prepolymer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

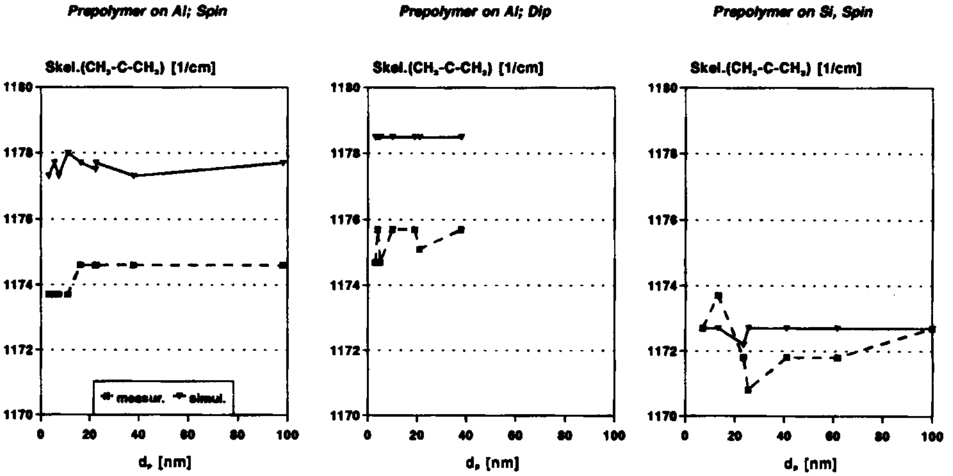

FIGURE 6 Simulated and measured positions for the skeletal vibration Skel $[C(CH_3)_2]$ of the *i*-propyl group *versus* prepolymer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

Surprisingly, the frequency shifts occur on the aluminium substrate over the entire thickness range up to 100 nm. On the other hand, Figures 6–8 do not reveal any significant frequency changes on the silicon substrate at all.

As noted above, the measurement on Si selects only the prepolymer transition dipoles with a component parallel to the interface. Hence, it can not be excluded that the transition dipoles directed perpendicularly to the silicon surface possess a frequency shift too. For the same reasons, it may be that on Al the moments parallel to the interface absorb light at the same frequencies as in the bulk.

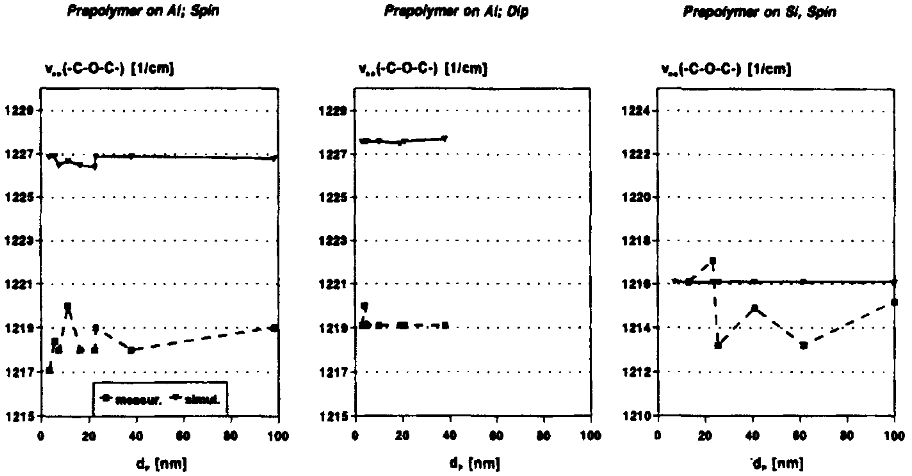

FIGURE 7 Simulated and measured band positions for the stretching vibration ν(C–O–C) of the (C–O–C)-bridge between triazine and benzene rings as a function of prepolymer layer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

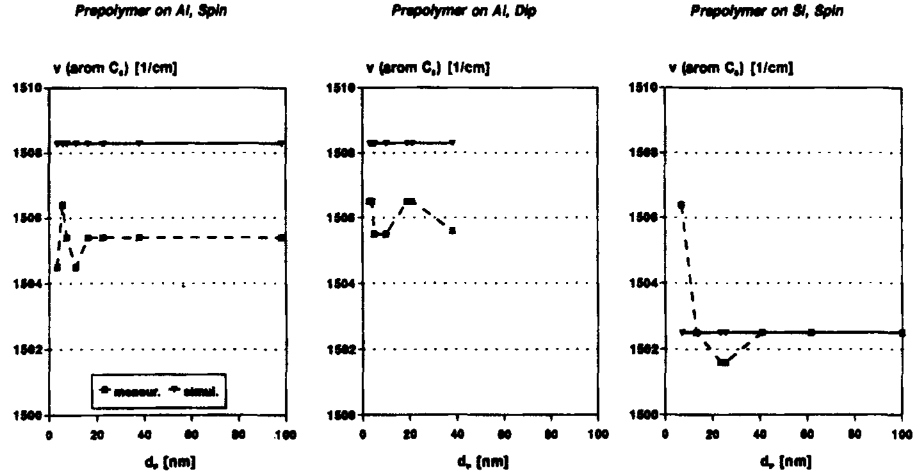

FIGURE 8 Simulated and measured band positions for the stretching vibration ν(arom C_6) of the benzene ring *versus* prepolymer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

In some cases, the relative intensity (referred to δ_{ip} (CH) in *p*-substituted benzene at 1015 cm^{-1}) of prepolymer bands depends on d_p in a way which is different from the corresponding d_p-function in the bulk-like films. In detail, the following results are found. The stretching vibrations of the cyanate group (*ca.* 2271 cm^{-1} and 2236 cm^{-1}) and its neighborhood in the benzene ring at about 1075 cm^{-1} reproduce the simulated data for all samples. Figure 9 provides an example for the d_p-dependence.

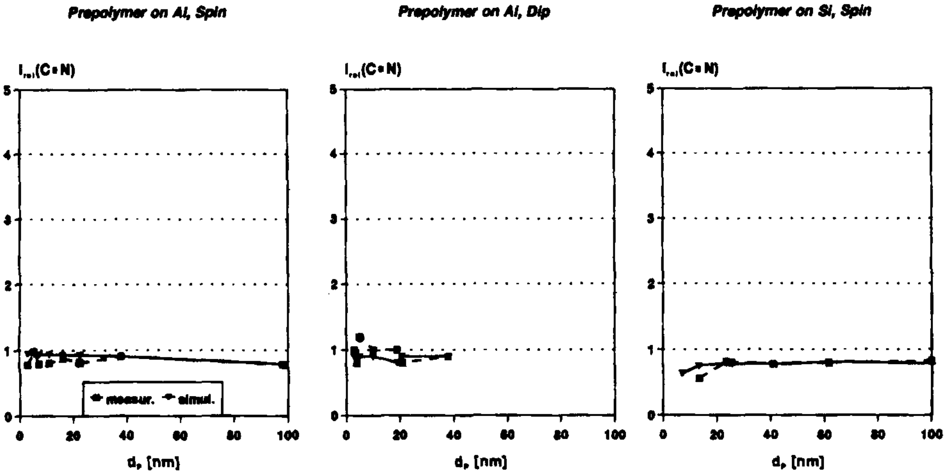

FIGURE 9 Simulated and measured relative intensity values of $\nu(C \equiv N)$ *versus* prepolymer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

The relative intensity of the i-propyl skeleton vibration corresponds on Si to the bulk behavior, see Figure 10. On Al, however, the measured data deviate weakly but systematically to larger values.

As compared with the simulation data, the experimental infrared absorptions of $\nu(\text{—}C_{\text{benzene}}\text{—}O\text{—}C_{\text{triazine}}\text{—})$, $\nu(\text{—}N{=}C\text{—})_{\text{triazine}}$ and ν (arom.C_6) lose more and more relative intensity on Al with decreasing d_p. Figures 11 and 12 provide examples of that behavior. The simulated intensity data increase with decreasing prepolymer thickness on Al. The intensity values measured on the very thin films grow much slower with decreasing d_p.

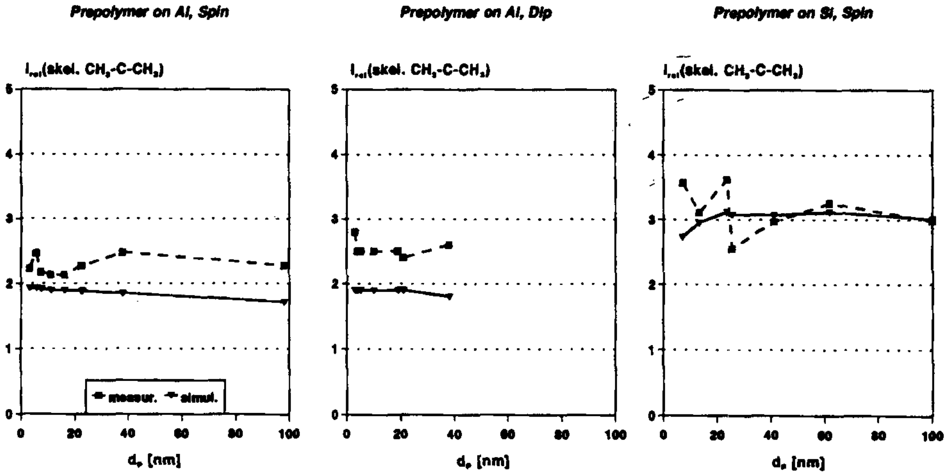

FIGURE 10 Simulated and measured relative intensity values of Skel $[C(CH_3)_2]$ *versus* prepolymer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

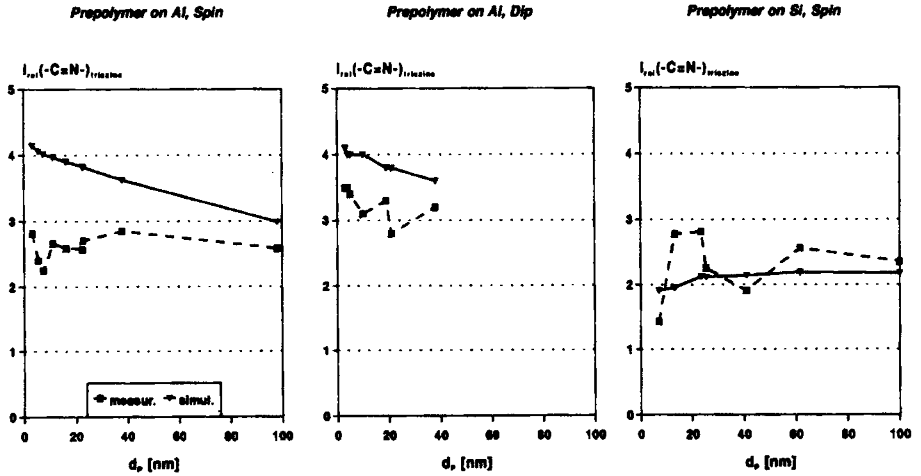

FIGURE 11 Simulated and measured relative intensity values of $\nu(-\mathrm{N}=\mathrm{C}-)_{\mathrm{triazine}}$ as a function of prepolymer layer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

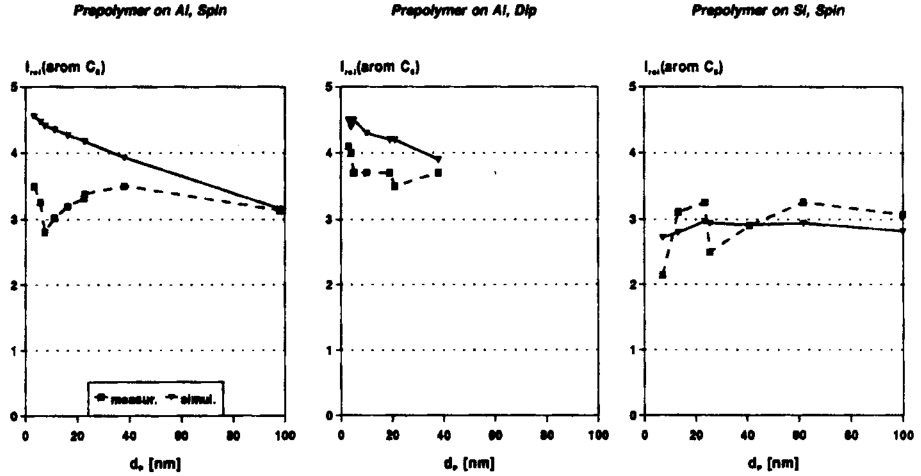

FIGURE 12 Simulated and measured relative intensity values of ν(arom. C_6) as a function of prepolymer layer thickness, d_p, for spin coating on Al and Si and dip coating on Al.

Below 40 nm, they even tend to fall with d_p. That difference between simulation and measurement appears clearly below 40 nm but it seems to extend over the whole thickness range. For the silicon substrates, the measured data reproduce the simulated bulk behavior within the experimental scatter.

A general view on all data for the Al substrate shows that the different preparation techniques do not produce any significant differences in the position or in the intensity of the infrared bands.

Finally, the reflection spectra provide no hint on a specific role played by the carbonaceous material that was detected by XPS on the bare substrates. As that contamination was present on both substrates it can not be responsible for the spectral peculiarities that have been observed on the aluminium only.

4. CONCLUSIONS

The described method of analysing infrared reflectance spectra provides information about the special physical state of thin organic films in contact with a solid. That information can be extracted with the help of spectra simulation using the optical functions of the bulk materials and the measured thickness values. The simulation yields spectra reflecting the sample response expected for pure bulk properties.

This analysis of reflectance spectra for DCBA prepolymer layers (*ca.* 2 nm to 100 nm) on the aluminium substrates reveals deviations from the bulk state for both the frequency and the relative intensity of selected absorption bands. The deviations are of varying strength and distribute over the whole mid-infrared. They are correlated to vibrations of the triazine ring and its surroundings. Vibrations of benzene rings and of the *i*-propyl groups are also involved. On the contrary, the cyanate group shows bulk properties in all layers.

The observed intensity reductions with d_p should be caused by concentration changes or by a preferential orientation. As the concentration is correlated to the composition of the prepolymer, the number of vibrating groups has to be considered. Figure 1 provides access to the problem. For the DCBA monomer, the number, *n*, of cyanate groups divided by the number of (CH)-groups in the benzene rings is

$$\frac{n(\mathrm{C}\equiv\mathrm{N})}{n(\mathrm{C}-\mathrm{H})\text{at arom. }\mathrm{C}_6}=\frac{1}{4}\quad \text{Monomer} \tag{1}$$

For the trimer, one obtains

$$\frac{n(\mathrm{C}\equiv\mathrm{N})}{n(\mathrm{C}-H)\text{at arom. }\mathrm{C}_6}=\frac{1}{8}\quad \text{Trimer} \tag{2}$$

Correspondingly, the pentamer provides a ratio of 1/10, the heptamer of 5/56, and so on. With the number distribution of the molecules, we get for the prepolymer

$$\frac{n(\mathrm{C}\equiv\mathrm{N})}{n(\mathrm{C}-\mathrm{H})\text{at arom. }\mathrm{C}_6}=\frac{0.765}{4}+\frac{0.125}{8}+\frac{0.046}{10}+\cdots\quad \text{Prepolymer} \tag{3}$$

That sum indicates any composition change. For the isotropic material, the ratio defined by Equation (3) is proportional to the measured intensity ratio

$$\frac{I[\nu(\mathrm{C}\equiv\mathrm{N})]}{I[\delta_{ip}(\mathrm{C}-\mathrm{H})\text{at arom. }\mathrm{C}_6]} \tag{4}$$

of these infrared bands. In Figure 9, the data measured for this ratio are equal to the bulk values. Thus, the prepolymer layers reproduce the bulk composition for both substrates and both preparation techniques. Moreover, the cyanate groups do not orient in a preferred direction.

Consequently, the intensity dependence on d_p observed in Figure 11 for the coatings on Al depicts a preferential orientation of the triazine grouping. At this point, further interpretation depends on detailed knowledge about the conformation states and the corresponding normal modes, including their transition dipole moments. In Section 3.1, a substantial lack of information was stated in this respect. Principally, molecular modelling techniques could fill the gap but that work is beyond the scope of this paper. The molecular properties of monomer and trimer are of special interest because they provide the majority of species in the prepolymer. Preliminary results for possible conformational states of the isolated molecule are given in Figure 13. They follow from quite simple calculations with the program MOBY.[27] The *i*-propyl group forms a "core" with the two benzene rings which is very stiff. The rotation of the cyanate group

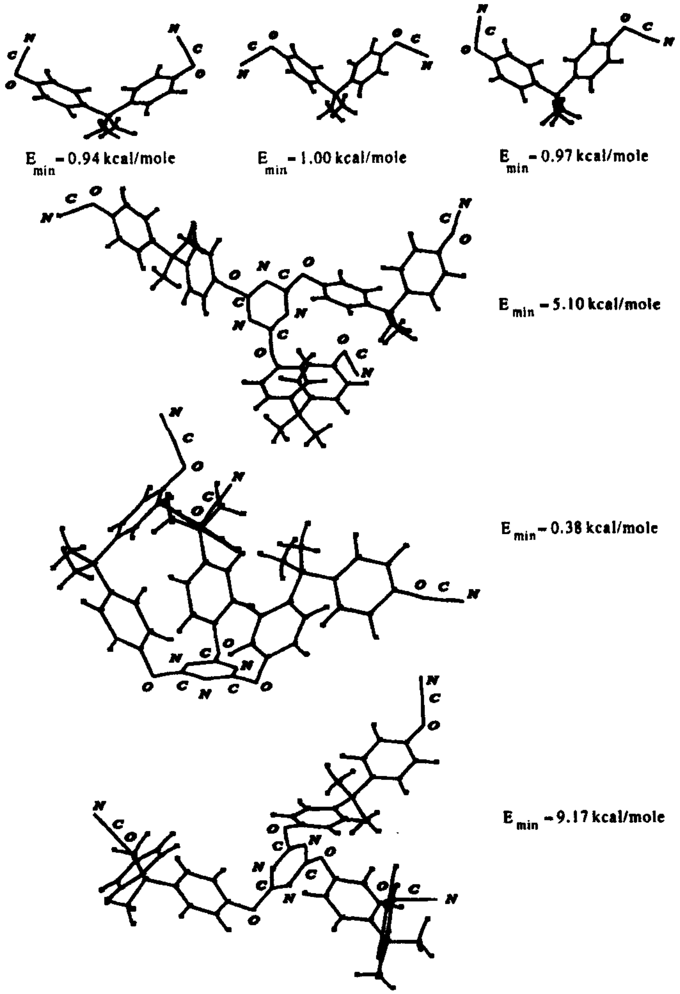

FIGURE 13 Calculated conformations of DCBA and cyclotrimer with low minimum energies, E_{min}, due to a combined quantum chemical (AM 1) and force field (AMBER) approach.

is considerably less hindered. The energy barriers between the different trimer conformations are very high. Thermally-activated conformation transitions seem very unlikely, therefore. That is also true for larger oligomers. Hence, the conformation distribution established in the melt during the polymerization should be conserved in the prepolymer. This distribution is not known yet and, hence, we can only speculate about the preferential orientation implied from the infrared spectra. As the triazine ring and the neighboring three oxygen atoms lie in the same plane, that should be also true for the transition moments of the $\nu(-N=C-)_{\text{triazine}}$ vibration and approximately for the $\nu(-C_{\text{benzene}}-O-C_{\text{triazine}}-)$ vibration. Therefore, the deficit of relative intensity established in Section 3.2 for the corresponding infrared bands means, in conjunction with the metal selection rule, that a considerable amount of triazine rings are oriented parallel to the interface. That effect is specific for the aluminium substrate. On the silicon substrate the triazine rings possess an isotropic distribution of orientation. Further, Figure 12 reveals a similar orientation effect for some benzene rings on Al. It cannot be decided yet whether the benzene rings at the triazine or the benzene at the cyanate groups are involved. That depends on the preferential conformation of the trimer and the larger oligomers.

Infrared absorption is commonly discussed within the model of the molecular oscillator. Due to this picture, the frequency reductions observed for the triazine grouping and for the *i*-propyl group in the thin films on Al are caused by diminished force constants or by increased effective masses. Each possibility depicts intermolecular interaction potentials that differ from the bulk. It should be underlined again that the frequency shift is measured only for those groupings that are not parallel to the interface. The reductions amount to 2–8 cm^{-1}. That corresponds to some 0.1–0.7% reduction of the vibration energy only. For experimental reasons, nothing can be said about the perpendicular orientation. The silicon substrate does not act on the parallel-oriented groupings.

It cannot be inferred from the infrared spectra alone what particular changes in the molecular state are responsible for the observed peculiarities in the thin prepolymer layers on aluminium with its native oxide layer. This is especially true with respect to their long range of at least 100 nm. For the moment, we state that the common adhesion theories hardly provide a plausible, straightforward explanation of the deduced interaction effect. Additional information has to be collected before a physical model is constructed.

Acknowledgement

This study was granted by the Volkswagen-Stiftung and by the BMFT (03C2012 3) in Germany. We thank Mrs. S. Jährig for doing the prepolymer synthesis and its molecular weight characterization. It is also a pleasure to acknowledge the XPS and AES investigations by S. Dieckhoff and V. Schlett, and the AFM characterization by T. Gesang that provided invaluable additional information on our samples. One of the authors (W.P.) is indebted to Professor Hatsuo Ishida from CWRU for the support during a stay in his laboratory in Cleveland, Ohio, U.S.A.

References

1. H. Ishida, *Rubber Chem. Tech.* **60**, 497 (1987).
2. F. J. Boerio, J. P. Boerio and R. C. Bozian, *Appl. Surf. Sci.* **31**, 42 (1988).

3. C. Carlsson and B. Liedberg, *Mikrochim. Acta* **1**, 149 (1988).
4. C. P. Trip and M. L. Hair, *Langmuir* **8**, 241 (1992).
5. R. A. Dluhy and D. G. Cornell, *ACS Symp. Ser.* (*FTIR Spectrosc. Colloid Interface Sci.* **447**, 193 (1990).
6. A. H. M. Sondag, A. J. W. Tol and F. J. Touwslager, *Langmuir* **8**, 1127 (1992).
7. M. K. Debe, *Progr. Surf. Sci.* **24** (1-4), 1 (1987).
8. R. O.Carter III, C. A. Gierczak and R. A. Dickie, *Appl. Spectrosc.* **40**, 649 (1986).
9. N. D. Schlotter, T. Bright and D. L. Allara, *SPIE* **553**, 494 (1985).
10. M. Grunze, W. N. Unertl, S. Gnanarjan and J. French, *Mat. Res. Soc. Symp.* **108**, 189 (1988).
11. H. G. Linde, *J. Appl. Polym. Sci.* **40**, 2049 (1990).
12. K. Konstadinidis, B. Thakkar, A. Chakraborty, L. W. Potts, R. Tannenbaum, M. Tirrell and J. F. Evans, *Langmuir* **8**, 1307 (1992).
13. M. Bauer and J. Bauer, in *Chemistry and Technology of Cyanate Ester Resins*, I. Hamerton, Ed. (Chapman and Hall, Glasgow, 1994), in press.
14. K. Fukui and T. Yamabe, *J. Polym. Sci.* **XLV**, 305 (1960).
15. Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik*, I. Band "Atom- und Molekularphysik", 2. Teil "Molekeln I" (Springer-Verlag, Berlin, Göttingen, Heidelberg, 1951).
16. H. J. Hediger, *Infrarotspektroskopie. Grundlagen, Anwendung, Interpretation*, Bd. 11 by F. Hecht, R. Kaiser, E. Pungor und W. Simon, *Methoden der Analyse in der Chemie* (Akadem. Verlagsges., Frankfurt a.M., 1971).
17. G. Sokrates, *Infrared Characteristic Group Frequencies* (J. Wiley and Sons, Chichester, New York, Brisbane, Toronto, 1980).
18. W. Brause, "Struktur- und H-Brückenbindungs–Untersuchungen an heterosubstituierten Nitrilen" Thesis, pp. 67–71, Zentralinst. Organ. Chemie, AdW der DDR, 1970.
19. V. A. Pankratov, V. V. Korshak, S. V. Vinogradova and A. G. Pucin, *Plaste und Kautschuk* **20**, 481 (1973).
20. G. Martin and R. Bacaloglu, *Organische Synthesen mit Cyansäureestern* (Akademie-Verlag, Berlin, 1980) pp.33–35.
21. D. A. Shimp, J. R. Christenson and S. J. Ising, *Prepr. SPI–Epoxy Resin Formulators Division Conference*, Hollywood, Florida, USA, 1990.
22. V. Hopfe and P. Klobes, *FSOS:IR-VIS-UV -Schicht- und Oberflächenpektroskopie*, TU Chemnitz, Sektion Chemie/Werkstofftechnik and Sektion Informatik, Carl Zeiss Jena GmbH, Forschungszentrum, 1990.
23. M. A. Ordal *et al.*, *Appl. Optics* **24**, 4493 (1985).
24. E. D. Palik (Ed.) *Handbook of Optical Constants of Solids* (Academic Press, New York, 1985).
25. V. Hofpe, "Erweiterung der Anwendungsbreite und Aussagefähigkeit optischspektroskopischer Untersuchungsmethoden für Festkörperoberflächen, Adsorbate und Schichtsysteme," Thesis B, TU Chemnitz, 1984.
26. P. H. Gaskell and D. W. Johnson, *J. Noncryst. Solids* **20**, 153 (1976).
27. U. Höweler, *MOBY-Molecular Modelling on the PC*, Vers. 1.5 (Springer-Verlag, Berlin, Heidelberg, 1992).