Study of the Structure of Polymers by Infrared Spectra

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Synopsis

In this review a short outline of the results of the application of IR-spectroscopy to the study of polymer physics is summarized. Questions of rotational isomerism, mechanical deformation of polymers, crystallization, intramolecular order, and microtacticity determination are discussed. Details are given on the authors' data concerning polypropylene, 1,4-*trans*-polybutadiene, poly(methyl methacrylate), and cellulose triacetate, and also data on calculations of spectra for different conformations of poly(vinyl chloride), poly(vinyl bromide), and poly(ethylene terephthalate).

Vibrational spectra, which play such a major role in the study of the structure and transformations of small molecules, are no less important for the investigation of polymers. Basically, it is a question here of infrared absorption spectra, since it is difficult to obtain good Raman spectra of polymers. A large number of polymers of both synthetic and biological origin have now been studied by infrared spectroscopy, and these investigations have made it possible to answer many fundamental questions concerning the physics of polymers.[1-3]

In this paper we shall report some of the results of work which has been carried out in the course of several years in the Laboratory of Polymer Structure, Institute of High Molecular Weight Compounds, Academy of Sciences, USSR. The problems in polymer physics which are solvable with the aid of infrared spectra can be classified as follows:

(*a*) The establishment of the chemical structure of macromolecules, i.e., the determination of the functional groups of atoms in the chain, the nature of their bonding, etc.

(*b*) The study of intramolecular short-range order in the sequence of monomers in a macromolecular chain. Here the most important problem is in the determination of the microtacticity of the macromolecule, i.e., in finding the relative composition and order of isotactic and syndiotactic links in the chain.

(*c*) The study of the rotational isomers of the macromolecule. The rotational isomers are of fundamental significance here, since the basic physical properties of polymers are, in the final analysis, determined by them (see below).

(*d*) In connection with problems *b* and *c*, the solution of the problem

of the secondary structure of the polymer—the intramolecular long-range order—is particularly important for stereoregular polymers and biological polymers (albumins and nucleic acids). This concerns the nature of the helical structure of the macromolecule as a whole.

(e) The study of intermolecular ordering of chains in bulk matter. This orientation is inherent in crystalline polymers, and there is local order, apparently, also in amorphous polymers. The physical and mechanical properties of polymer materials depend in an essential way on the intermolecular (and also, of course, the intramolecular) ordering.

(f) The study of changes in the intramolecular and supermolecular structure of a bulk polymer during changes in its state—crystallization, vitrification, swelling, and also upon stretching of the polymer.

In order to solve these physical problems it is necessary to develop a theory of macromolecular vibrational spectra, i.e., to do research in the field of theoretical spectroscopy. A theory is necessary which permits the calculation and interpretation of the frequencies, intensities, and polarizations of the infrared bands of ordered and nonordered polymeric chains. It is also needed for a discussion of the heat capacities of polymers. A theory of the spectra of crystalline polymers which explains the "crystalline bands" is of special interest.

Let us discuss certain questions associated with problems c and e. According to the rotational isomerism theory,[4,5] which was proposed by one of the present authors, a statistical discussion of the physical properties of macromolecules can be based on the idea of rotational isomerism. A macromolecule in the equilibrium state represents a mixture of rotational isomers; each link in the chain can exist in the form of several discrete conformations, the free energies of which, generally speaking, are different. The existence of rotational isomerism in polymers has actually been observed experimentally by the use of infrared spectra in the investigations of Novak[6] and other authors. The energy differences of the rotational isomers are close to those of similar low molecular weight compounds. Thus, for polyethylene the value $\Delta E \simeq 700$ cal./mole of the links has been found from the temperature dependence of the intensities of infrared bands; this value is close to the corresponding quantity for n-butane.

The rotational isomerism theory makes possible a molecular interpretation of the stretching of polymers and of the mechanism of the high elasticity of rubbers. In the stretching of a macromolecule by an external force there occurs a redistribution of rotational isomers along the chain and a transition of rotational isomers with short links into isomers with long links. This is a cooperative process since the realization of a certain conformation of a given link depends on the conformations of neighboring links. Accordingly, a theoretical analysis of the stretching of rubber, as well as a calculation of the physical properties of macromolecules, requires the use of the Markov chain method, which in this case utilizes the so-called Ising model.[5]

It follows from the theory that in the stretching of a polymer there

occurs a rotational isomerization i.e., a change in the relative content of rotational isomers.   High elasticity is, then, a result of this situation, which has been completely verified experimentally by a spectroscopic study of polymer films in polarized infrared light.   A change in the content of rotational isomers was observed in the stretching of polyethylene and poly(vinyl acetate),[7] natural rubber,[8] and with particular clarity in the stretching of gutta-percha, which is accompanied by a considerable change in the spectrum.[4,5]   Thus infrared spectroscopy gives very valuable information here.   More recently, independent verifications of the rotational isomerism theory of the stretching of rubber were obtained by Flory and his co-workers in studying the thermomechanical properties of polymers.[10]

Problems *e* and *f* are closely associated with rotational isomerism.   The crystallization of a polymer is a manifestation of the stabilization of a definite rotational isomer.   During crystallization substantial changes occur in the infrared spectrum.   Thus, in the transition from amorphous to crystalline polyethylene, bands appear at 720 and 730 cm.$^{-1}$, the intensity of the 1308 cm.$^{-1}$ band decreases, and the 1460 cm.$^{-1}$ band splits into bands at 1464 and 1473 cm.$^{-1}$.[11,12]   Sutherland and co-workers[12,13] have shown that the appearance of the doublets at 720, 730 cm.$^{-1}$ and 1464, 1473 cm.$^{-1}$ is caused by a resonance interaction of deformation vibrations of CH_2 groups in the crystal unit cell.   However, the polarization of the split components obtained in these studies does not agree with observation. It has subsequently been shown that the nature of the splitting and the polarization of the bands can be explained only by considering not just the closest but also the more distant hydrogen atoms of neighboring chains.[14] The indicated changes in the spectrum of polyethylene can be used successfully for a quantitative determination of the degree of crystallinity.

In the melting of crystalline, isotactic polypropylene, the 841, 997, and 1167 cm.$^{-1}$ bands disappear.   In hardened, amorphous polypropylene the differential intensities of these bands are less than for a crystalline sample, but for the 973 and 1153 cm.$^{-1}$ bands they are the same.[15]   The 973 cm.$^{-1}$ band is retained also in solution.   It is obvious that the 841, 997, and 1167 cm.$^{-1}$ bands are determined by intermolecular ordering and the 973 and 1153 cm.$^{-1}$ bands by intramolecular ordering, i.e., by the helical structure of a macromolecule of isotactic polypropylene.   The Raman spectra of this polymer were also obtained in our laboratory.   In the crystalline polymer, lines at 842 and 812 cm.$^{-1}$ are observed, but in the melted state only the 812 cm.$^{-1}$ line is present.   In the infrared spectrum only one component of the doublet is active (841 cm.$^{-1}$).

The bands which are characteristic of the crystalline state of a polymer can be observed very well in the spectra of polyamides.   During crystallization the intensities of the 833, 928, 959, and 1028 cm.$^{-1}$ bands increase, and the intensities of the 777, 914, 976, and 1000 cm.$^{-1}$ bands decrease.[16,17] Changes in the spectrum of poly(ethylene terephthalate) which occur when it crystallizes are explained not by a resonance interaction but by changes in the set of rotational isomers.   Actually, similar changes are observed in
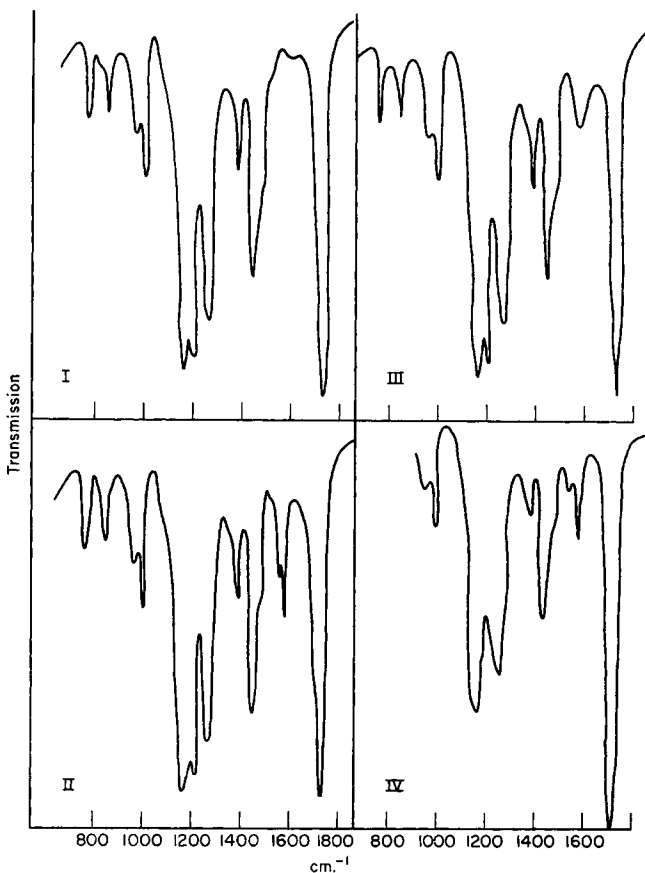
Fig. 1. Infrared absorption spectra of isotactic poly(methyl methacrylate) films: (*I*) amorphous; (*II*) crystallized; (*III*) crystallized and heated to 220°C.; (*IV*) crystallized and dissolved in chloroform. Cell thickness $d = 0.250$ mm., concentration $\sim 1.27\%$.

the stretching of an amorphous polymer. In the infrared spectrum of amorphous, isotactic poly(methyl methacrylate) a weak band is observed at 1580 cm.$^{-1}$. Upon crystallization it splits into two components at 1560 and 1580 cm.$^{-1}$. It is noteworthy that both these bands persist in a chloroform solution of the previously crystallized polymer[18] (Fig. 1). They persist also during melting of the crystalline polymer, the 1560 cm.$^{-1}$ band gradually disappearing at temperatures which substantially exceed the melting point. One can imagine that the splitting of the 1580 cm.$^{-1}$ band in the crystalline state is associated with an intramolecular resonance interaction in the ordered helical parts of the chain. The persistence of the effect in solution and in melting indicates either the extreme slowness of the isomerization of the nonequilibrium ordered state of the chains or the nonequilibrium of the original amorphous polymer. Two crystalline modifications of 1,4-*trans*-polybutadiene exist. The first of these is stable up to
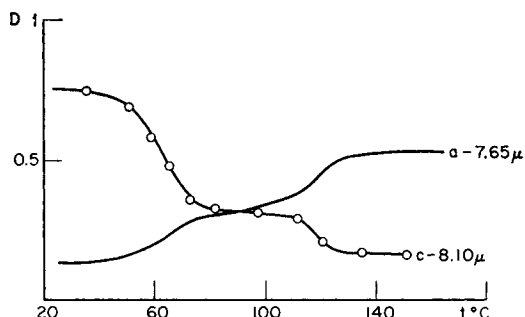
Fig. 2. Variation in optical density of 8.10 μ crystalline band (c) and 7.65 μ amorphous band (a) with temperature.

a temperature of 50°C.; in the range 50–70°C. the two modifications co-exist; from 70°C. up to the melting point of 130°C. only the second exists. The crystalline bands of this polymer are located at 774, 1055, 1235, and 1335 cm.$^{-1}$, and their intensities decrease with increasing temperature. On the other hand, the intensities of the amorphous bands at 1309 and 1349 cm.$^{-1}$ increase upon heating. The temperature dependence of the optical density of the bands at 1235 and 1309 cm.$^{-1}$ is given in Figure 2.[19] The observed picture explains the transition from modification I to II and the melting of the latter. The results are in agreement with x-ray data.

One may consider that the crystalline bands, which do not completely disappear even during melting, and the amorphous bands of the polymer are associated with the appropriate rotational isomers.

When cellulose triacetate is crystallized by annealing at 220°C., several changes are observed in its infrared spectrum.[20] The spectra of crystal-lized, amorphous cellulose triacetate and crystallized cellulose triacetate which has been dissolved in chloroform are given in Figure 3. Crystalliza-tion leads to the appearance of bands at 436, 490, 526, 548, 565, 1050, and 1074 cm.$^{-1}$. The low frequency bands are apparently associated with acetyl groups, since absorption is also observed in this region in ethyl acetate. The 1050 and 1074 cm.$^{-1}$ bands must be assigned to valence vibrations of C—O groups.

The appearance of a series of bands in the spectrum of crystalline cellu-lose triacetate can be explained by intermolecular ordering brought about by the resonance interaction of macromolecules located in the same unit cell of the crystal.

We have presented several examples of polymers which we have inves-tigated. In all cases we meet the interesting and important spectroscopic problem of the origin of crystalline and amorphous bands in the spectrum of the polymer.

A theoretical analysis of the problem naturally begins with a calculation of the spectrum of a macromolecular chain. The first approximation here consists of considering the chain to be completely ordered, i.e., a linear
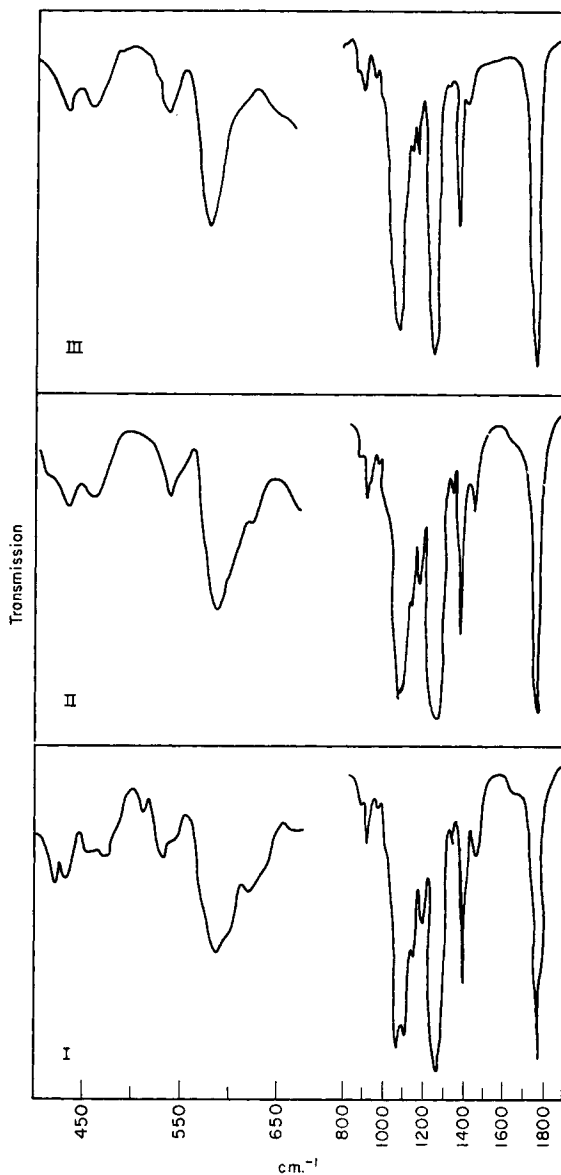
Fig. 3. Infrared absorption spectra of cellulosetriacetate films: (*I*) heat-treated; (*II*) not heat-treated. Film thicknesses in the region 400–650 cm.$^{-1}$ were 50 μ, and in the region 800–1800 cm.$^{-1}$ were 15 μ. Curve *III* is cellulosetriacetate dissolved in chloroform; concentration of the solution was 1%, cell thickness was 0.25 mm.

crystal. This approximation can be used successfully in the study of crystalline polymers in which the chain is actually ordered and also in the study of amorphous polymers whose chains may contain separate, rather long portions with configurations similar to those of crystals.

In a second approximation separate fragments of the chain are selected for which calculations are then performed. Clearly this approximation is considerably easier for groups located within the fragment than for terminal groups. It is particularly convenient for treating the effect of rotational isomerism on the spectrum of the polymer.

We have performed calculations of frequencies for polyethylene,[21] poly(vinyl chloride),[22] and poly(vinyl bromide)[23] in the first approximation. The second approximation was used for poly(vinyl chloride) and also poly-(ethylene terephthalate),[24] the calculations being made for fragments of the chain which corresponded to different stereoisomers and rotational isomers. In all cases force constants were used which were calculated from data pertaining to small molecules of similar structure. Good agreement with experiment was achieved. In the case of poly(vinyl chloride) the C—Cl valence vibrations were considered in detail for various chain configurations. The calculations confirm the assumption made in many works that the α-band of the C—Cl valence vibration (690–700 cm.$^{-1}$) refers to a folded rotational isomer in both the isotactic and the syndiotactic polymers. The β-band (635–640 cm.$^{-1}$) and δ-band (605 cm.$^{-1}$) belong to regular syndiotactic parts of the chain. The wide γ-band (615 cm.$^{-1}$) is assigned to vibrations of short parts of the chain. The calculation of these vibrations was done for a model chain consisting of two types of oscillators: one of them was the model for the C—Cl bond and the other for the group of angles and bonds through which neighboring C—Cl bonds interact. The parameters of these effective oscillators (masses and force constants) were determined from exact solutions of the problem for fragments and for long chains.

By considering finite portions of different lengths, we obtain a set of frequencies forming a wide band which is comparable with the experimentally observed 615 cm.$^{-1}$ band.

We have also calculated vibration frequencies for a fragment of the poly(ethylene terephthalate) macromolecule. Such a calculation is of particular interest in view of the fact that, as already mentioned, the behavior of certain bands (1440 and 1470 cm.$^{-1}$, 1370 and 1340 cm.$^{-1}$) with increasing degree of crystallinity indicates possible rotational isomerism. The calculation, which was done for the *trans*- and the folded conformations of the fragment —OCH$_2$—OCH$_2$—, shows that the computed values of the frequency differences of the bending and wagging vibrations of the CH$_2$ groups (25 and 30 cm.$^{-1}$) are in good agreement with the experimental data. This makes it possible to assign the 1445 and 1370 cm.$^{-1}$ bands, which are particularly intense in the amorphous polymer, to bending and wagging vibrations of the CH$_2$ group in the folded conformation, and to assign the 1470 and 1340 cm.$^{-1}$ bands, whose intensities increase with increasing crystallinity, to the corresponding vibrations in the *trans* conformation.

In order to study the stretching of polymeric fibers and films it is necessary to use polarized infrared spectroscopy. Infrared dichroism gives valuable information about the stereochemical structure of polymers.
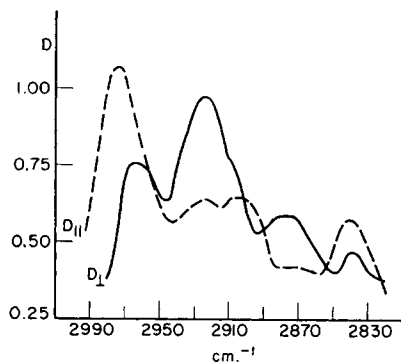
Fig. 4. Dichroism of polypropylene in the region 2900–2800 cm.$^{-1}$: (———) electric vector perpendicular to stretch axis; (--) electric vector parallel to stretch axis.

An analysis of steric interactions in the polymeric chains ($-CH_2-$CHR$-)_n$ shows that those conformations are energetically most favorable which are realized in the corresponding crystalline structures.[25,5] A given crystal structure is determined not by intermolecular but by intramolecular interactions. As has already been stated, a considerable degree of short-range order, which corresponds to long-range order in a crystal, is preserved in the amorphous state and even in solution. In the oriented portions of stretched chains a short-range order corresponding to the crystalline conformation for a given type of stereochemical structure is preserved. The orientation of the dipole moment for a given vibration relative to the axis of the oriented portion is determined by the structure of the polymer. The existence of a short-range order between vibrations in adjacent monomeric units can lead to a resonance splitting of bands which also depends on the structure of the polymer.[26]

We have carried out experimental investigations of the infrared dichroism for samples of polypropylene of different microtacticity.[27,28] The spectrum of polypropylene which has been stretched (10–12 times) at a temperature of 150°C. contains bands at 2845, 2875, 2900 (weak side band), 1926, and 2970 cm.$^{-1}$ in the region of the CH valence vibrations. When samples with a considerable degree of isotacticity are stretched, a distinct splitting (10–12 cm.$^{-1}$) of the 2970 cm.$^{-1}$ band is observed. The split components have different polarizations in agreement with the theoretical predictions (see Fig. 4). There is no such splitting in a sample with little isotacticity.

The 2845 and 2926 cm.$^{-1}$ bands of the symmetric and antisymmetric CH_2 valence vibrations are not split but do possess noticeable dichroism. The dichroism is measured by the quantity

$$R = (\epsilon_\pi - \epsilon_\sigma)/(\epsilon_\pi + 2\epsilon_\sigma)$$

where ϵ_π and ϵ_σ are the absorption coefficients for light polarized parallel and perpendicular to the axis of orientation of the film respectively. The

ratio R_{2845}/R_{2926} is very sensitive to the degree of isotacticity of the sample (see Table I).

TABLE I
Dependence of R_{2845}/R_{2926} on the Stereoregularity of the Sample

Polypropylene fraction	R_{2845}	R_{2926}	R_{2845}/R_{2926}
Hexane	0.05	−0.06	−0.82
Heptane residue	0.04	−0.12	−0.36
Octane residue	0.04	−0.18	−0.23

Here the degree of isotacticity increases in going from top to bottom. Theory predicts the following values of R_{2845}/R_{2926}: for isotactic 3_1-helixes, $0:(-1)$; for the planar syndiotactic portions, $(-1):(-1)$; for syndiotactic chains consisting of 4_1-helixes, $(-1):(+^1/_2)$. Experiment leads to a strong negative dichroism for the 2926 cm.$^{-1}$ band and to a small positive dichroism for the 2845 cm.$^{-1}$ band, which basically corresponds to an isotactic structure. The observed small positive value of dichroism for the 2850 cm.$^{-1}$ band and the dependence of the ratio R_{2845}/R_{2926} on the degree of isotacticity is probably determined by the presence of syndiotactic "joints" between the isotactic sequences. The CH_2 groups in these joints can be oriented at angles close to 90° relative to the basic isotactic helical portions. In this case a symmetric CH_2-vibration will possess positive dichroism.

Thus infrared dichroism gives valuable information about the micro-tacticity of macromolecules.

In spite of the indicated successes of theory and experiment, there is not yet a consistent quantitative theory of the origin of crystalline bands in polymers. Crystalline polymers are highly imperfect molecular poly-crystals. Polymers almost never crystallize completely. The spectral theory of such systems involves great difficulties which have still not been surmounted. Defects in a polymeric crystal lattice are determined pri-marily by the configurational diversity of its links, which is retained in the noncrystallized portions. Nevertheless, the basic reasons for the appear-ance of crystalline bands are clear. They are associated with a change in the selection rules upon transition from one rotational isomer to another and with resonance splitting caused by intramolecular and intermolecular interactions. This is splitting of the Davydov type.[29] Ever so many strict theoretical calculations have been carried out just for polyethyl-ene.[13,14] Obviously this problem is extremely important and interesting both for the physics of polymers and for molecular spectroscopy.

The limited space of this report does not permit us to dwell on the other important applications of infrared spectroscopy to the investigation of polymers—in particular, to the study of vitrification and swelling of poly-mers; these aspects have been discussed elsewhere.[30,31]

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Résumé

Dans cette revue on a résumé brièvement quelques applications de la spectroscopie I.R. pour l'étude de la physique des polymères. On discute des questions relatives à l'isomérie de rotation, de la déformation mécanique des polymères, de la cristallisation, de l'ordre moléculaire et de la détermination de la microtacticité. On donne des détails sur les résultats dus aux auteurs concernant de polypropylène, du 1.4-*trans*-polybutadiène, de polyméthacrylate de méthyle et du triacétate de cellulose, ainsi que les résultats rélatifs aux calculs effectués sur les spectres des différentes conformations du chlorure et du bromure de polyvinyle et du téréphtalate de polyéthylène.

Zusammenfassung

Im vorliegenden Überblick wird eine kurze Zusammenfassung der bei der Anwendung der IR-Spektroskopie auf Probleme der Polymerphysik erhaltenen Ergebnisse gegeben. Fragen der Rotationsisomerie, der mechanischen Deformation von Polymeren, der Kristallisation, der intramolekularen Ordnung und Mikrotaktizitätsbestimmung werden diskutiert. Über die vom Autor an Polypropylen, 1,4-*trans*-Polybutadien, Polymethylmethacrylat und Zellulosetriacetat erhaltenen Daten sowie über Ergebnisse von Berechnungen der Spektren für verschiedene Konformationen von Polyvinylchlorid, Polyvinylbromid und Polyäthylenterephthalat werden detaillierte Angaben gemacht.