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# Structural Study of Organic Polymers by the Microdiffraction Electron Microscope Method

T.M.Babchinitser and L.G.Kazaryan

The advances achieved by the method of electron microdiffraction in the study of the crystal structures of organic polymers with the aid of the transmission electron microscope are examined and the advantages and disadvantages of the method are analysed. It is shown that the diffraction studies on polymers in a transmission electron microscope not only supplement X-ray data but in many cases provide unique possibilities for structural analysis. The applied aspect of the structural studies of polymers is examined and methods are described for the preparation of the specimens and for protecting the polymeric object from the action of radiation.
The bibliography includes 122 references.

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## I. INTRODUCTION

Modern electron microscopy (EM) has an enormous potential, providing great possibilities for the study of the microstructures and compositions of substances and materials.[1] The structural motif of the crystal at the level of the detailed atomic structure can be visualised on high-voltage instruments. The method for the recording of electron diffraction in a selected region—electron microdiffraction (EMD), which carries information about the crystal structure, has been brought to a high degree of perfection. The EM results are supplemented by using spectroscopic-analytical devices (analysis of the energy losses by electrons, dispersion of energy, and emission—X-ray, Auger, etc.); all the elements ranging from sodium to uranium can be detected. Electron microscopy has begun to be used in crystal-chemical studies on polymers, which are difficult objects for EM because of their lack of resistance to radiation damage by the electron beam.

When transmission electron microscopy (TEM) is used for the solution of structural problems in polymer chemistry, it has now become possible to achieve in practice simultaneously the recording of the EMD pattern and of the image of the corresponding section of the object under the conditions of light and dark fields. Quantitative analysis of the data makes it possible to determine the structure of the crystalline region of the polymer, including the chain conformation with the coordinates of the atoms and the packing of the macromolecules. When the reflection intensities on the electron diffraction pattern are used, both experimental and computational–theoretical problems arise. As regards the experimental technique, there is the question of the development of standard methods for the preparation of the specimens which do not introduce artefacts into the investigation and which are suitable for obtaining an electron diffraction pattern with a high information content. This includes the problems of protecting the object against radiation damage and of increasing the quality of the EMD pattern, the accuracy of the measurements, etc. Problems of another kind include those of justifying the application of the kinematic approximation to the calculation of the structural diffraction amplitudes, the development of methods for the determination of the chain conformation, etc. These questions are considered in the present review, whose aim is to discuss the possibilities and advances achieved by the EMD method in structural research into organic polymers.

## II. THE INFORMATION CONTENT AND VALIDITY OF THE RESULTS OF THE STRUCTURAL STUDY OF POLYMERS BY ELECTRON MICRODIFFRACTION

The theoretical principles of electron diffraction have been described in the monographs of Pinsker,[2] Vainshtein,[3] Cowley,[4] etc. In relation to TEM, the theory and practice of the use of the EMD method have been examined in a series of monographs and manuals by Soviet and foreign authors.[5-12] However, virtually no attention is devoted in these publications to the study of polymers and only Fischer's review,[5] published in 1964, is wholly devoted to this question. Specific data, characterising the contribution of the EMD method to structural research into polymeric compounds by the beginning of the 1980's, have been described in a report to a symposium of the American Chemical Society.[13]

It is noteworthy that, in relation to polymers, the electron diffraction method is relatively new and has developed "in the footsteps" of X-ray diffraction; therefore, in view of the aims of this review, it is useful to consider briefly the general postulates characterising the similarity and differences between electron and X-ray diffraction.

The information content in the electron diffraction pattern is determined primarily by the fact that (as in the case of X-rays) it makes it possible to recreate the molecular and atomic structure of a substance by means of calculations based on the concept of the inverse space of the crystal. In assessing the possibilities of the electron diffraction method, it must be emphasised that the electron microscope has undoubted advantages over the electron diffractometer, making it possible to combine the analysis of the diffraction pattern with the visual study of the microstructure of the corresponding section of the object. This is especially effective in the direct resolution of the crystal lattice.

In the microdiffraction mode of the operation of the transmission electron microscope, one obtains electron diffraction patterns of three main types depending on the phase state of the polymer: ring patterns (from polycrystalline specimens), point or arc patterns (from single crystal specimens), and texture patterns (from axially extended films and fibres).

An electron diffraction pattern of the first type indicates the crystallisation of the polymer and makes it possible to characterise the structure of the crystalline region by a set of interplanar spacings. The electron diffraction pattern of a single crystal consists of one of the planar sections through the inverse lattice; for the complete representation of the inverse lattice in order to determine the geometry of the unit cell, it is necessary to obtain a series of diffraction patterns for different orientations of the specimen relative to the incident beam. A texture electron diffraction pattern with arc reflections along the equator and layer lines is formed when the incident beam is directed at right angles to the extension axis of the specimen and represents either the entire or almost the entire inverse lattice making it possible to calculate the crystallographic parameters and the repeat period of the macromolecule.

The first stage of the microdiffraction study yields structural characteristics such as the space group, the unit cell parameters, the volume and density of the unit cell, the number of monomer units, and the number of chains in the cell. Furthermore, the determination of the intensities of the reflections and calculation of the experimental structural diffraction amplitudes yield information for the determination of the chain conformation and the atomic coordinates and also of the molecular packing by mathematical procedures widely developed previously in relation to X-ray diffraction. The two diffraction methods are similar both as regards the nature of the physical processes and the methodology of the treatment of the experimental data, although they have their advantages and limitations due to the characteristics of the radiation and of the experimental techniques.

X-Rays are scattered by the electron clouds of atoms, while electrons are scattered by the potential generated by the atomic nuclei and their electron clouds. The advantages of electron diffraction are associated primarily with the much shorter wavelength of the electrons, which depends on the accelerating potential:

$$\lambda = h/(2meV)^{1/2} = 12.225/V^{1/2},$$

where $h$ is the Planck constant, $m$ the mass of the electron, $V$ the accelerating potential, and $e$ the electronic charge. The non-relativistic wavelength of the electrons at an accelerating potential of, for example, 100 kV or 1 MV is 0.037 and 0.0087 Å respectively, while the wavelength of X-rays is 1.54 Å (copper anode, $K_\alpha$ line). High-voltage microscopes with accelerating potentials ranging from 500 to 3000 kV have now been developed, which possess a whole series of unique possibilities, in particular they make it possible to raise the resolution on the image (which depends on the wavelength) to the atomic-molecular level.

In connection with the appreciably shorter wavelength, the region of the inverse space of the crystal detected by the EMD method has expanded sharply, on the one hand, and the energy of the interaction of the radiation with the substance has increased, on the other. The characteristic features of the scattering of electrons on passage through the object result in a much greater number of reflections in the diffraction pattern and their intensity is $10^6$–$10^8$ times greater than in the scattering of X-rays. For example, structural analysis by the electron diffraction method makes it possible to determine the positions of the hydrogen atoms, although the ratio of their structural amplitudes to the amplitudes of the carbon atom is much higher than in X-ray diffraction.

Apart from the fundamental advantages indicated above, there are also preparative advantages, namely electron microscopy makes it possible to investigate single microcrystals of the polymer, while the X-ray diffraction method operates mainly with macrospecimens in an oriented crystalline state; therefore the EMD method provides a unique possibility for the structural study of crystalline polymers which are incapable of orientational stretching. When the polymer can be obtained in the form of an oriented crystalline specimen, the possibility of obtaining the electron diffraction pattern of a single crystal together with a texture electron diffraction pattern and a texture X-ray diffraction pattern is also extremely important, since it makes it possible to overcome a series of disadvantages which lower the information content of the experimental data for the texture.[14] The disadvantages of the difraction pattern of the axial texture include the small number of Bragg maxima and the relatively low intensity, which has an especially negative effect on the reflections which require a high resolution; furthermore, a partial loss of reflections is observed owing to their overlap and disappearance against the diffuse scattering background due to the amorphous regions of the specimen.

The electron diffraction patterns of single crystals are free from the above limitations. They exhibit a greater number of reflections in the basal plane and their intensity is higher, which increases the information content of the diffraction data and in particular it makes it possible to refine the character of the systematic extinctions.[13] For example, in the study of poly(trimethylene terephthalate) it was shown[15] that the X-ray diffraction pattern of the fibre has 5–10 equatorial reflections with $hk0$ indices, while the electron diffraction pattern of a single crystal contains at least five times more reflections due to the basal plane, from which the space group and the unit cell parameters were determined acurately.

As regards the comparison of the X-ray and electron diffraction patterns of the axial texture, both methods provide analogous information, although the higher intensity of the reflections on the remote layer lines of the texture electron diffraction pattern makes it possible to determine more accurately the repeat period of the macromolecule.[16] It is noteworthy that the advantages of the texture electron diffraction patterns were elucidated already at an early stage in the development of electron diffraction and were demonstrated in a study[17] of the structure of cellulose.

The disadvantages of the EMD method are caused primarily by the fact that the electron microscope equipment is much more complex than the X-ray diffraction equipment and much more stringent requirements must be met by the technical state of the microscope, the correct focusing of the objective, the quality of the calibration of the apparatus constant, etc. Furthermore, the probability of error increases as a consequence of the effect of radiation on the microspecimen. For example, in the study of the structure of poly(trifluoroethylene) it was established[18] that the damage of the specimen on irradiation leads to unduly high unit cell parameters compared with X-ray diffraction data. The authors of special manuals on practical electron microscopy have arrived at the unambiguous conclusion that the accuracy of measurements based on electron diffraction patterns with the maximum possible prevention of errors is at least to within 0.1% of the measured interplanar spacings. One of the most important factors governing the improvement of accuracy is the calibration of each electron diffraction pattern by the vacuum sputtering of a test object (TlCl, Au, Al) on the electron microscope grid holder.

The fundamental problem of taking into account the dependence of the intensity of the reflections on structural amplitudes arises in structural analysis based on electron

diffraction data.[3,4,8] The corresponding calculations in electron diffraction studies are carried out in terms of the so called kinematic theory of the scattering of waves by crystals. This presupposes that, under the influence of the primary beam, each atom becomes a source of secondary spherical waves, whose amplitude is much smaller than the amplitude of the initial wave. The scattering process is not accompanied by a change in wave length and there is no repeated scattering of the waves already scattered or such scattering may be neglected. Being propagated in all directions with phase relations determined by the geometry of the relative positions of the scattering centres, the secondary waves interfere with one another and determine the overall intensity of the reflections. However, since in the absence of X-rays the electrons strongly interact with the substance, the application of the kinematic theory is limited by the conditions stipulating a small thickness of the crystal (100–150 Å) and the absence of its bending on the support. Otherwise the intensity of the diffraction maxima may be influenced by dynamic scattering, i.e. by the repeated scattering of the already scattered electrons.

The two-wave approximation of the dynamic theory presupposes that only two waves—primary and diffracted–interact in the crystal. The multiwave theory takes into account both the multiple interaction of the diffracted waves and the finite size of the object, the different energy losses, etc. The role of dynamic scattering increases if the molecule contains heavy atoms and also with increase in the accelerating potential. Cowley,[19] Goodman and Moodie,[20] as well as Dorset and Moss[21–23] have been concerned with the influence of dynamic scattering on structural diffraction amplitudes. In relation to the analysis of diffraction by thin and deformed crystals of paraffins, the last workers demonstrated that the kinematic theory of scattering can be adopted as a suitable approximation in the calculation of the atomic structure, but in each specific case it is necessary to check the influence of the dynamic scattering in order to complete the investigation and to obtain a reasonable agreement between the experimental and calculated structural amplitudes.

## III. ADVANCES AND PROSPECTS IN THE APPLICATION OF THE MICRODIFFRACTION METHOD TO THE DETERMINATION OF THE CRYSTAL STRUCTURES OF ORGANIC POLYMERS

The first studies on polymers by the electron diffraction method were carried out by Soviet workers using an electron diffractometer at the beginning of the 1950's.[24–28] Precision studies involved the determination of the structure of a synthetic polypeptide—poly(γ-methyl-L-glutamate)[29] and the refinement of the atomic coordinates (including hydrogen) in the poly(ethylene terephthalate) macromolecule.[30] There is no doubt that studies at this level prepare the ground, as it were, for the development of quantitative microdiffraction methods.

Systematic studies on organic polymeric compounds by the TEM method began at the end of the 1950's and the possibility of microdiffraction observations was already used in the first classical investigations by Till,[31] Keller,[32] and Fisher.[33] The results obtained by the EMD method played an important role in the development of ideas about the characteristic features of the crystallisation of macromolecules[34–36] and the hypothesis of the folding of polymer chains was put forward on the basis of the electron diffraction patterns of a thin film of guttapercha long before the start of systematic research into the crystallisation of polymers.[37] However, the problem of applying EMD to the structural analysis of polymers was not formulated and solved until 1974 when Claffey et al. demonstrated the possibility of using the reflection intensities in the electron diffraction pattern of a single crystal in a study of poly[3,3-di(chloromethyl)-oxacyclobutane].[38] The authors were able to confirm the X-ray diffraction data for the cell geometry, to refine the space group, and to determine the atomic coordinates and the conformation of the side chains.

The crystal structures of polymers according to electron microdiffraction data.

| No. | Polymer | Unit cell parameters | Chain conformation | *R* factor | Refs. |
|---|---|---|---|---|---|
| (I) | Poly(*p*-oxyphenylene-*m*-carbaboranyl) | Orthorhombic; $a = 11.40$, $b = 7.70$, $c = 18.0$; $\rho_c = 1.29$, $\rho_a = 1.17$; $z = 4$, $n = 2$ | — | — | [39] |
| (II) | Poly(dipropylsiloxane) | Tetragonal; $P4_3$, $a = 9.52$, $b = 9.40$; $\rho_c = 1.015$; $z = 4$, $n = 1$ | $H(4/1)$ | — | [40] |
| (III) | Poly[diphenyl(phenyl-*p*-tolyl)siloxane] | Orthorhombic; $a = 21.06$, $b = 10.53$, $c = 10.36$; $\rho_c = 1.17$; $z = 8$, $n = 2$ | $H(4/1)$ | — | [41] |
| (IV) | Poly(phenyl-*p*-tolylsiloxane) | Orthorhombic; $a = 21.0$, $b = 10.86$, $c = 9.97$; $\rho_c = 1.24$; $z = 8$, $n = 2$ | $H(4/1)$ | — | [41] |
| (V) | Poly(vinylidene fluoride), γ-form | Monoclinic; $a = 4.96$ $b = 9.67$, $c = 9.20$; $\gamma = 93°$ | $P(T_2GT_2\bar{G})$ | — | [42] |
| (VI) | Poly(bistrifluoroethoxyphosphazene) | Monoclinic; $a = 10.03$, 3, $b = 9,37$, $c = 4,86$; $\gamma = 91°$ | — | — | [43] |
| (VII) | Poly(bisphenoxyphosphazene) | Monoclinic; $a = 16.6$, $b = 13,8$, $c = 4,91$; $\gamma = 83°$ | — | — | [43] |
| (VIII) | Poly(*p*-oxybenzoyl) | Orthorhombic; $P2_12_12_1$ or $P222_1$, $a = 7.62$, $b = 5.70$, $c = 12.56$; $\rho_c = 1.46$; $z = 4$, $n = 2$ | $P(2/1)$ | — | [44 45] |
| (IX) | Poly[3,3-bis(chloromethyl)oxacyclobutane], α-form | Orthorhombic; $Pna2_1$; $a = 17.85$, $b = 8.15$, $c = 4.78$; $z = 4$, $n = 4$ | $Z(TT)$ | 0.247; $N = 20$ | [38] |
| (X) | Poly(ethylene sulphide) | Orthorhombic; $a = 8.508$, $b = 4.93$, $c = 6.686$; $z = 4$, $n = 2$ | $P$ | 0.33; $N = 20$ | [14] |
| (XI) | Cellulose triacetate | Orthorhombic; $P2_12_12_1$, $a = 24.68$, $b = 11.52$, $c = 10.54$; $z = 8$, $n = 4$ | $H(2/1)$ | 0.26; $N = 40$ | [48] |
| (XII) | Poly(trimethylene terephthalate) | Triclinic; $a = 4.637$, $b = 6.266$, $c = 18.64$; $\alpha = 98.4°$, $\beta = 93.0°$, $\gamma = 111.1°$, $\rho_c = 1.138$, $z = 2$, $n = 1$ | $P(TGGT)$ | 0,255; $N = 25$ | [15] |
| (XIII) | Poly(β-oxybutyroyl) | Orthorhombic; $P2_12_12_1$; $a = 5,76$, $b = 13.2$, $c = 5,96$; $z = 2$, $n = 2$ | $H(2/1)$ | 0,33; $N = 28$ | [49] |
| (XIV) | Poly(hexamethylene terephthalate), form I | Triclinic; $P\bar{1}$, $a = 5.217$, $b = 5.284$, $c = 15.738$; $\alpha = 12.94°$, $\beta = 9.76°$, $\gamma = 95.6°$, $z = 1$, $n = 1$ | $P$ | 0.172; $N = 19$ | [13. 50. 51] |
| (XV) | Poly(hexamethylene terephthalate), form II | Triclinic; $a = 5.217$, $b = 10,568$; $c = 15.738$; $\alpha = 129.4°$, $\beta = 97.6°$, $\gamma = 95°$, $\rho_c = 1.278$; $z = 2$, $n = 2$ | $P$ | 0.161; $N = 19$ и 0.196; $N = 24$ | [50. 51] |
| (XVI) | Poly(hexamethylene terephthalate), form III | Monoclinic; $a = 9.10$, $b = 17.56$, $c = 15.74$; $\alpha = 127°$; $z = 6$, $n = 6$ | $P$ | — | [50 51] |
| (XVII) | *trans*-Polyacetylene | Orthorhombic; $Pna$, $a = 7.32$, $b = 4.24$; $c = 15.74$; $\rho_c = 1.13$; $z = 4$, $n = 2$ | $Z(2/\bar{1})$ | 0.24; $N = 23$ | [52] |
| (XVIII) | Poly(*p*-xylylene), β-form | Trigonal; $P3$, $a = 20.53$, $c = 6.55$; $\gamma = 120°$; $\rho_c = 1.58$; $z = 16$, $n = 16$ | $P$ | 0.21; $N = 25$ | [53. 54] |
| (XIX) | Poly(2,4-*trans*-cyclohexanediyldimethylene succinate) | Monoclinic; $P2_1n$, $a = 6.486$, $b = 9.482$, $c = 13.51$; $\beta = 45.9°$; $\rho_c = 1.259$; $z = 2$, $n = 2$ | $P(GGTT)$ | 0.199; $N = 87$ | [55. 56] |
| (XX) | Poly(dodeca-1,11-diyne) macromonomer | Monoclinic; $P2_1/n$, $a = 13.25$, $b = 14.15$, $c = 7,63$; $\beta = 118.5°$; $z = 2$, $n = 4$ | $P$ | 0.13; $N = 17$ | [57] |
| (XXI) | Product of solid-phase polymerisation of the macromonomer (XX) | Monoclinic; $P2_1/n$, $a = 9.17$, $b = 12.25$, $c = 9.92$; $z = 4$, $n = 4$ | $P$ | 0.13; $N = 36$ | [57] |

Notation: $\rho_c$ is the density of the crystal, $\rho_a$ the density of the amorphous specimen, $z$ the number of units in the unit cell, $n$ the number of chains in the unit cell, $N$ the number of reflections on the electron diffraction pattern; the following notation has been adopted for the chain conformation: $H$ = helix, $P$ = planar, $Z$ = zigzag, $T$ = *trans*, and $G$ = *gauche*.

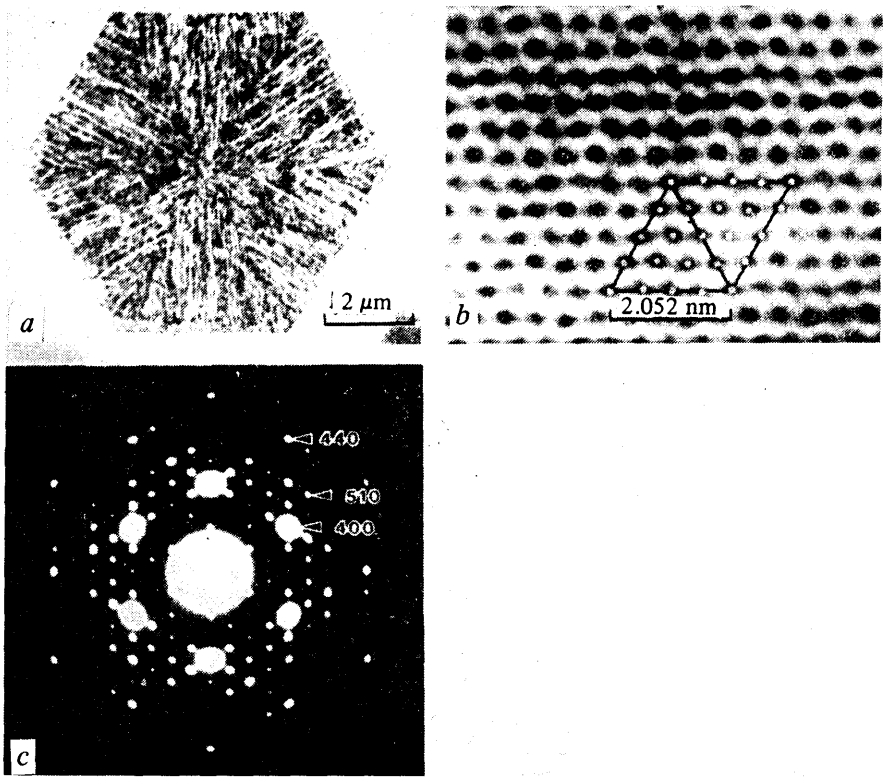



**Figure 1.** The electron microscope study of poly(*p*-xylene):[53] *a*) single crystal of the β-form; *b*) image of the crystal lattice obtained with the aid of a high-voltage microscope having a resolution of 0.20–0.15 nm; each dark spot corresponds to the projection of the macromolecule onto the basal plane and the white circles indicate the position of the macromolecules in the unit cell; *c*) electron diffraction pattern of a single crystal of the β-form; the numerals denote the indices of the corresponding reflections.

One of the most important results of their study[38] was the demonstration of the applicability of the kinematic approximation to the calculation of structural diffraction amplitudes. This study influenced the general level of electron microscope investigations of polymers and opened up ways to the use of TEM as a method for structural analysis. Since its publication,[38] more than 10 years have elapsed, but one must conclude that the development of research on these lines is relatively slow evidently due to the experimental difficulties in the preparation of the objects and the determination of electron diffraction patterns of a sufficiently high quality and with an adequate information content; the main bulk of the determinations of the structure of polymers are therefore carried out at the present time by the X-ray diffraction method. On the other hand, in recent years there have been undoubted advances in the use of EMD.

The advances achieved with the aid of EMD can be analysed by means of a Table which presents the most accurate studies demonstrating the level of modern research and the characteristic range of objects. The publications included in the Table can be divided into two groups—those carried out without taking into account the reflection intensities in the electron diffraction pattern for compounds (I)–(VIII) and those using them in order to carry out a complete structural analysis of compounds (IX)–(XXI).

In the studies of the first group, the determinations were made of the space group, of the unit cell parameters, and of the packing elements and, for compounds (II)–(IV), (V), and (VIII), the hypothesis concerning the chain conformation was justified. The value of studies of this kind consists primarily in the fact that the structures of the compounds investigated cannot be studied by X-ray diffraction because neither oriented specimens nor sufficiently large crystals can be obtained for such compounds. Polymers of this type include poly(*p*-oxyphenylene-*m*-carbaboranyl),[39] poly(dipropylsiloxane),[40] and also weakly orientable poly(diarylsiloxanes).[41] All the polymers enumerated were first investigated with the aid of EMD. Poly(vinylidene fluoride) had been studied earlier by X-ray diffraction but the controversy concerning the structure of its γ-form extended over a decade and it was shown that mechanical deformation leads to a polymorphic transformation (the transition from the γ-form to the β-form). The study of single crystals with the aid of the electron microscope, which rules out the necessity for the mechanical deformation of the specimen, made it possible to determine unambiguously the structure of the γ-form and also to observe the phase transition to the ε-form on thermal annealing of crystals of the γ-form.[42]

Analysis of the examples presented in the Table shows that polymers whose properties have attracted attention have been most often the objects of electron microscope studies. Such objects include, for example, the class of polyphosphazenes, forming liquid crystal systems, whose representatives are poly(bistrifluoroethoxyphosphazene) and poly(bisphenoxyphosphazene).[43] Poly(*p*-oxybenzoyl) also has interesting properties,[44,45] because its copolymers with other polyesters

make it possible to obtain liquid crystal systems.[46,47] This polymer was first investigated in 1976, but the structure proposed for the double helix was not confirmed by other physical methods. A precision reinvestigation carried out in 1984 made it possible to correct the initial data and to determine unambiguously the crystal structure of the compound.[45]

In assessing the advances achieved with the aid of the EMD method in polymer chemistry on the basis of the results of compounds (IX)–(XXI) (see Table), one may conclude that this method permits crystal-chemical determinations whose aim is to establish the atomic structure and the molecular packing of high-molecular-weight compounds. A number of compounds of this group had been investigated earlier by the X-ray method. These include poly[3,3-di(chloromethyl) oxacyclobutane],[38] poly(ethylene sulphide),[14] cellulose triacetate,[48] poly(β-oxybutyroyl),[49] polyesters of terephthalic acid and aliphatic glycols,[13,15,51,52] and also *trans*-polyacetylene.[52] For these polymers, the results of EMD studies confirmed, revised, or supplemented the existing X-ray diffraction data. In other cases, the structure of the compound was determined for the first time by the EMD method, for example, those of poly(*p*-xylylene),[53,54] poly(1,4-*trans*-cyclohexanediyldimethylene succinate),[55,56] and poly(1,11-dodecadiyne).[57]

When the total structural analysis of the polymer by the EMD method is carried out, this problem is greatly facilitated in those cases where data are available for the structures of the individual fragments of the polymer unit and the way that they are linked together. The structures of low-molecular-weight compounds serving as models of the monomer units of the macromolecules have been determined for this purpose. For example, the structure of cellulose triacetate has been deduced from data on the structure of the trimer.[48] Dimethyl terephthalate and the diphenyl ethers of the corresponding glycols have been investigated as models of the units in polyesters.[15,49–51] An analogous procedure has been used in the study of poly(1,4-*trans*-cyclohexanediyldimethylene succinate).[55,56]

A number of the publications presented in the Table reveal very great advantages of diffraction electron microscopy in the study of polymorphism. Thus it has been found that the texture X-ray diffraction pattern of poly(hexamethylene terephthalate) contains reflections from several polymorphic phases which are superimposed and cannot therefore be used to establish the structure of each of these phases. On the other hand, in the study by the TEM method the crystals of each phase have their own characteristic form and give rise to an individual EMD pattern; furthermore, in the polymer

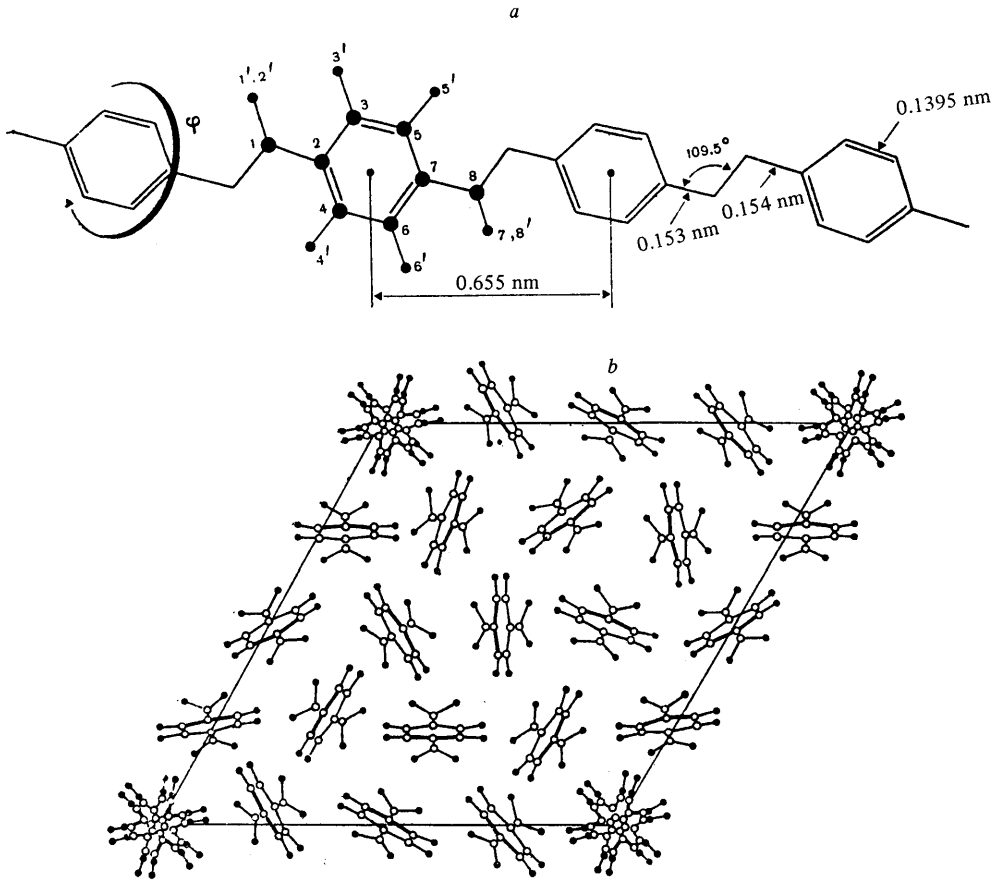



**Figure 2.** The molecular structure of poly(*p*-xylylene): *a*) *trans*-zigzag conformation of the macromolecule with a repeat period of 0.655 nm; $\phi = 90°$ is the angle between the plane of the benzene ring and the plane of the $-CH_2-CH_2-$linkage; *b*) three-dimensional structure of a single crystal of the β-form in projection onto the basal plane; the filled and open circles denote carbon and hydrogen atoms respectively; the unit cell contains 16 macromolecules, one of which assumes one of three equivalent positions in accordance with the *P*3 symmetry.

phase I it is possible to distinguish two similar structures. Separate analysis of electron diffraction patterns of single crystals made it possible to characterise all three polymorphic phases [(XIV)–(XVII), Table] and to index fully the reflections on the X-ray diffraction pattern. The problem of isolating one of the polymorphic phases has been solved also for poly(*p*-xylylene) [(XVIII), Table] in an investigation by Japanese workers,[53,54] which demonstrated the high level of the advances in the application of TEM to the study of polymers. Electron microscopes of two types were used—with a potential of 80 kV (JEM-7) and a high-voltage microscope (JEM-500). In both cases images of both the microstructure and of the EMD pattern were obtained (Fig.1). The structure of the β-form with an *R*-factor of 0.21 was analysed on the basis of quantitative microdiffraction data; the application of the high-voltage instrument enhanced the local nature and the resolution of the EMD patterns and also reduced the radiation damage during the recording of the pattern. A series of focal photomicrographs with a resolution of 1.5–2 Å were obtained. The photomicrographs, representing a direct resolution of the crystal lattice of the β-form, were treated by the optical filtration method. The optical diffractometer trace for the image coincided with the EMD pattern of the single crystal.

The resolution of the interplanar spacings on the photomicrograph was achieved for polydiacetylene single crystals on the basis of 1,6-di(*N*-carbazolyl)hexa-2,4-diyne[58] and also poly(*p*-phenyleneterephthalimide).[59] However, only in the case of poly(*p*-xylene) did the combination of the analysis of the high resolution image and the EMD patterns lead to the determination of the chain conformation and the atomic coordinates and to the discovery of the characteristic features of the molecular packing in the crystal (Fig.2).

The methodological procedures in the crystal-chemical determinations of the structures of polymeric compounds are extremely individual and depend to a large extent on the complexity of the structure of the object and the completeness of the available experimental data. A general approach to the solution of the problem usually involves the conformational analysis of the postulated model, which makes it possible to determine the chain parameters influencing the repeat period and also the internal energy of the system. Then the conformation in best agreement with experimental data is selected by trial and error. Apart from conformational analysis the Fourier synthesis of the electron density has been used, for example, by Claffey et al.[38] and Roche et al.[48]

The model is refined by the method of least squares, familiar from X-ray diffraction, modified for the determination of the structure of the macromolecule by introducing stereochemical limitations.[60,61] The method involving the minimisation of the packing energy[62] and the combination of the two methods mentioned[63] are also used. The *R* factor defining the agreement between the calculated theoretical and experimental structural diffraction amplitudes in accordance with the formula[8]

$$R = \sum_{hkl} \| \Phi_e | - | \Phi_t \| \Big/ \sum_{hkl} | \Phi_e |,$$

where $\Phi_e$ are the observed structural amplitudes and $\Phi_t$ are the theoretical structural amplitudes for the proposed model, serves as the criterion of accuracy.

As can be seen from the corresponding columns in the Table, in modern studies the *R* factor is approximately 0.3 to 0.2, which indicates a fairly high accuracy of the results, bearing in mind the complexity of the macromolecule as an object of structural study.

Much attention has been devoted in studies of compounds (IX)–(XXI) to the validity of the application of the kinematic approximation to the calculation of structural diffraction amplitudes. Claffey et al.[38] proposed the agreement between the results of EMD and X-ray diffraction and also a weak influence of dynamic scattering on the R factor in test calculations as validity criteria. In a special appendix to a communication concerning the study of the structure of poly(1,4-*trans*-cyclohexanediyldimethylene succinate),[56] it was shown that ideal single crystals 100 Å thick are bent by not more than 2° and that dynamic scattering exerts only a weak influence on the *R* factor. In a study of poly(hexamethylene terephthalate), no bending of the crystals whatever was observed.[50] Under these conditions, the kinematic theory is fully applicable.

It must be emphasised that, in selecting the section for microdiffraction study, it is essential to employ a combination of the light field and the dark field modes of the operation of the electron microscope in order to choose suitable crystals. In the studies quoted above special attention was devoted to the reproducibility of the experimental results and to the accuracy of the measurements of the intensities. For this purpose, several tens of EMD patterns were photographed and the intensities were measured with the aid of automatic scanning microphotometers.

## IV. THE PRACTICAL VALUE OF THE RESULTS OF STRUCTURAL STUDIES ON POLYMERS

Analysis of publications on the structural analysis of polymers by the EMD method has shown that in such investigations the authors endeavour to relate the characteristics of the structure of macromolecules to the physicochemical properties of the materials. Thus in a study of poly(trimethylene terephthalate), it was established[15] that the aliphatic fragment of the chain has the *trans*, *gauche*, *gauche*, *trans*-conformation and that the transition from the *gauche*-to the *trans*-conformation does not require much expenditure of energy, which accounts for the high capacity of this material for orientational stretching. As a result of a study of tolyl-substituted poly(diarylsiloxanes), it was found[41] that, with increase in the number of substituents in the benzene ring, the crystallographic cell parameters are altered, which increases the interchain distance; in its turn, this improves the solubilities and lowers the melting points of the materials.

A characteristic example of the direct relation between the structural results and the solution of problems of practical importance is provided by the study of the structure of polyacetylene. It has been shown that the conductivity of the material depends on the ratio of the *cis*- and *trans*-isomers and that only the latter isomer is thermodynamically stable.[52,64] Evidently, the knowledge of the structural characteristics of each isomer is extremely important for the solution of the problem of the specific influences on the properties of the materials in the synthesis of the polymer and its subsequent doping. However, the X-ray diffraction data obtained are controversial because of the thermodynamic instability of the *cis*-isomer and also because of the dependence of the structure of the compound on the polymerisation catalyst used. Furthermore, polyacetylene films cannot be made into highly oriented objects, which limits the scope of X-ray diffraction.

The electron microscope method provides much more information in the study of the structure of polyacetylene, since it makes it possible to carry out its formation reaction directly on the electron microscope grid, the fibrillar crystals giving rise to a high quality texture electron diffraction pattern. The first studies on these lines were performed in 1980.[65] Then Shimamura et al.[52] were able to carry out a complete structural analysis and to obtain the crystallographic characteristics of the *trans*-isomer (XVII) (see Table), which were then confirmed also in other investigations.[66,67] In

1984 Dickenson et al.[68] studied the isomerisation of polyacetylene directly on the electron microscope grid and proposed a method for the determination of the *cis*–*trans*-isomeric composition of the polymer with the aid of EMD patterns. Simultaneously with the study of the structure of polyacetylene, the investigation of the doped materials by the EMD method was begun. Analysis of the studies on polyacetylene shows that, although they have not yet been completed and the structural data are so far contradictory,[69] nevertheless the electron microscope method is irreplaceable in the investigation of the initial polymer and of the conducting materials based on it.

Yet another example of the large amount of information derivable by the microdiffraction method is provided by the investigation of the solid-phase polymerisation of diacetylenes. The structural analysis of poly(dodeca-1,11-diyne) and of the insoluble product obtained by its γ-irradiation has been carried out.[57] This study led to interesting conclusions about the mechanism of structure formation in the final product (XXI). Namely, it was shown that the reaction involving the cross-linking of the chains is of the solid-phase type, because a secondary product is formed following a slight rotation and migration of the molecules along the crystallographic *c* axis when the closest packing of the parallel layers of polymer chains is achieved. This was indicated by the absence of a change in the space group and by the decrease in the volume of the unit cell of the crystal.

An electron microscope study of polydiacetylene based on 1,6-di(*N*-carbazolyl)hexa-2,4-diyne has been carried out (using TEM, scanning EM, and high-resolution TEM), which made it possible to obtain crystallographic data and a direct image of the structural motif of the crystal.[58] Polydiacetylene based on 2,4-hexadiynylene bistoluene-*p*-sulphonate was investigated in solid-phase polymerisation on the electron microscope grid[70] and also directly in the chamber of the electron microscope.[71] In the latter case it was claimed that the results of the investigation are of practical interest for the preparation of photoresistors. An important structural result of the studies of the solid-phase polymerisation of diacetylenes is the demonstration of the formation of fully straightened chains distributed in the plane of lamellar and fibrillar crystals.[70]

An application of electron microscopy with practical importance involves the study of the structure of highly modular thermostable fibres of the type of poly(*p*-benzamide)[59] and poly(*p*-phenylenebenzothiazole).[72] The crystal structures of these compounds have been investigated, by X-ray diffraction, but the joint application of scanning and transmission EM (the light and dark field of modes, EMD) also helped to elucidate the structural organisation of these materials which determines their unique properties.

Thus one may conclude that the importance of the microdiffraction method consists not only in the determination of data on the structures of the crystalline regions of polymers, but also in the possibility of using the structural results for the solution of applied technological problems.

## V. MODERN SOLUTIONS OF EXPERIMENTAL PROBLEMS INVOLVING THE APPLICATION OF THE ELECTRON MICRODIFFRACTION METHOD TO THE STUDY OF POLYMERIC COMPOUNDS

The success of the structural analysis of polymers depends in many respects on the solution of a series of experimental problems, such as, for example, the preparation and correct recording of data for the test objects. As shown above, electron diffraction patterns of single crystals have the highest information content (based on the resolution of the reflections and their intensities). A general method for the preparation of single crystals involves crystallisation from solutions and systematic studies of the structures of polymers were begun with its aid.[31–33] In the Soviet Union this field was pioneered by members of Kargin's School.[73–75] Various methods of crystallisation from solutions were developed by the end of the 1970's. These methods are characterised by two main procedures: the use of highly dilute solutions (0.001–0.1%) and rigorously controlled crystallisation temperatures. The long crystallisation period, necessary for the preparation of perfect crystals, is noteworthy (for example, several days in the crystallisation of polyacrylonitrile[76] or even several weeks in the case of isotactic polystyrenes[77]). Even readily crystallising polymers, such as, for example, poly(*p*-xylylene) (XVIII) (see Table), have to be maintained at the crystallisation temperature for several days.

The method and mechanism of crystallisation from solutions have been examined in greatest detail in the paper of Blundel et al.[78] and in Keller's review.[79] It was shown that, in the course of repeated dissolution and precipitation of polymers, a crystallisation "memory" is retained in the form of the spontaneous formation of nuclei on which the macromolecules are recrystallised. There exists a limiting redissolution temperature at which the crystals formed have a monolayer character with a perfect habit and a uniform thickness even at a relatively high concentration of the initial solution (0.1%), although an increase in concentration usually complicates the morphology of the supermolecular formations. For example, the temperature of the primary dissolution of polyethylene in xylene was 120 °C and was determined visually from the transparency of the solution and by dilatometric measurements. On cooling to 75 °C, exhaustive crystallisation occurred with appearance of turbidity in the solution, which again became transparent at 98 °C. Repeated isothermal crystallisation at temperatures in the range 98–105 °C led to the formation of perfect crystals giving rise to a distinct EMD pattern. This method is general for the crystallisation of polymers from solutions, naturally with an individual selection of crystallisation temperatures. It has been used in studies on the crystallisation of compounds (IV), (V), and (IX)–(XVI).

For polymers which are readily soluble in organic solvents and which are not precipitated from the solution on cooling, hot concentrated solutions are mixed with a suitable amount of precipitant. This procedure was proposed in early studies[58,59,80] and is again used nowadays, for example, in the preparation of polymers such as derivatives of polyphosphazene (VI) and (VII) (see Table). A difficult feature of the method is the need to eliminate the possibility of contact between the polymer and an excess of the precipitant, which is achieved by rigorous stirring or by breaking the tube with the solution in the flask containing the precipitant. Polymers also crystallise when solutions are cooled very slowly, for example, at a rate of 0.5 K $h^{-1}$ and less, as was done in the crystallisation of poly(ethylene terephthalate).[81]

In carrying out crystallisation from solution, one should bear in mind that polymers can form solvates with the solvent.[82,83] A specific feature of the solvates is the breakdown of their crystal structure after the removal of the solvent or after its replacement by another liquid, as a result of which the diffraction patterns of the electron microscope preparation vanish.[64,84] In order to rule out the possibility of the formation of solvates in the preparation of perfect polymer single crystals, it is necessary to use mixtures of a poor solvent with the precipitant and a high crystallisation temperature. It is then also essential to subject the suspensions to hot filtration with subsequent drying *in vacuo*.[85]

A simpler method of preparation of single crystals has been proposed.[66,86] It actually consists in isothermal crystallisation from a dilute solution in an atmosphere of the solvent

itself. The authors of these investigations obtained polyethylene, polypropylene, isotactic polybut-1-ene, polyacrylonitrile, and cellulose triacetate single crystals in the following manner: a glass plate attached to a string was lowered vertically into a thermostatted solution of the polymer and, after being kept there for a short time, was removed with the aid of a mechanical device at a rate of 1 cm $h^{-1}$; after it had risen fully, the plate was kept for a further 1 h in the solvent vapour, the polymer film was transferred to the surface of water by a standard method, and was fished out onto the grid holder. This method has not come to be widely used but it has been tested successfully on a series of polymers, for example, in the crystallisation of carbaborane-containing polyesters and polydiarylsiloxanes (I), (III), and (IV) (see Table).

The preparation of electron microscope objects, synthesised by solid-phase polymerisation, is also closely related to methods of crystallisation from solution. The question of preparing almost defect-free polymer single crystals by the topochemical polymerisation of diacetylene derivatives has been examined in a review,[87] which also includes electron microscope results. The usual method of preparation of the objects [for example, compound (XIX)—see Table] involves the initial growing from the solution of perfect monomer crystals in the form of lamellae[57] or needles,[59,69] which are deposited on a grid holder with a carbon support and are then subjected to various types of treatment to polymerise them, for example $\gamma$-irradiation from a $^{60}CO$ source. Similar methods have been used in the preparation of polyacetylene (XX) specimens (see Table): a solution of the catalyst is deposited on the grid with the support, dried, cooled to −78 °C, and maintained in a stream of acetylene at a pressure of 3–5 mmHg for 20 s; the *cis*-isomer is converted into the *trans*-isomer by heating the object on the grid at 200 °C for 2 h.[52]

In the preparation of crystals from solution, an extremely important stage involves the deposition of the object on the grid holder, because kinematic scattering conditions break down not only when the thickness of the crystals increases but also when they are bent. It has been shown that the best support for the preparation may be a thin carbon film, although it does in fact increase the diffuse background on the image and on the EMD patterns.[52,54] The orientation of the crystals on evaporation of the solution can be specified by the surface of the base, for example, the cleavage surface of NaCl or mica. A precision study by this method has been carried out[42] [compound (V)—see Table]. It was shown that, in the thermal crystallisation of poly(vinylidene fluoride), epitaxial growth in two mutually perpendicular directions is observed on the NaCl surface. Analysis of the EMD patterns of the object crystallised on mica and on the NaCl surface, with the aid of goniometric measurements, yielded information for the most accurate determination of the crystallographic parameters of the $\gamma$-phase.

As already stated in Section II, the texture electron diffraction patterns of films or fibres can be used in addition to the electron diffraction patterns of single crystals for the determination of the crystal structures of polymers. The development of methods for the orientational crystallisation of thin polymer films was dictated not only by the need to determine the molecular structure but also by the possibility of investigating the supermolecular structures of partly crystallised specimens under low-angle diffraction conditions. We shall not deal with this field of study, but procedures for the preparation of oriented crystalline specimens for electron microscopy have been described.[88–90]

The methods of preparation of thin oriented films have been described for poly(vinylidene fluoride),[91–93] poly(alkaneimides),[16] poly(diarylsiloxanes) [compounds (III) and (IV)—see Table] and poly(ethylene sulphide) (X). In the main, the preparation of the specimens reduces to casting thin films from dilute solutions (0.5–0.25%) and their monoaxial stretching with simultaneous or subsequent annealing at a temperature close to the glass point. This procedure involves considerable experimental difficulties in view of the small thickness (and hence low strength) of the films. Miniature devices in the form of frames of different design, to which the films are attached by adhesion on being withdrawn from water, are used for stretching. Devices for stretching in the microscope itself have also been proposed.[94] It is noteworthy that many investigations prefer to use the primitive method involving the stretching of the films on water with the aid of forceps[95] or on glass in a softened state with the aid of a spatula. For example, during this preparation procedure, it has been possible[14] [compounds (X)—see Table] to obtain the EMD pattern of a film of crystalline oriented poly(ethylene sulphide), which was suitable for complete structural analysis (in combination with electron diffraction patterns of single crystals). The polymer can also be subjected to deformation not only by stretching the specimen but also by shear, as has been done, for example, in the study of poly(*p*-phenyleneterephthalimide)[96] and also polyacetylene.[97]

Whereas the preparation of oriented crystalline films presents major difficulties to the investigator, the study of the structures of crystalline fibres is greatly facilitated, since in this case one can use the ultrasonic dispersion method with subsequent deposition of the object on grid holders with a support. Dispersion methods and devices have been described in practical manuals.[98] As an example of the use of dispersion in EMD studies, one may quote the investigations of highly modular thermostable fibres.[59] An unexpected result was obtained in the preparation of a poly(*p*-oxybenzoyl) (VIII) specimen, where the dispersion of the initial powder made it possible to observe in the electron microscope both polymer crystals and fibres giving rise to a texture electron diffraction pattern.

In addition to the methods described, mention should be made of the preparation of replicas and subsequent removal of the test substance, which had been proposed already at an early stage of the development of electron microscopy[99,100] and has been used successfully in modern research.[101]

Apparently the most complex method for the preparation of polymer specimens involves the use of an ultramicrotome, because it can be accompanied by the mechanical deformation of the specimens and the introduction of artefacts into the investigation. This method has been developed mainly for the study of biological objects and has been described in special manuals.[102] One of the first objects investigated by the EMD of thin sections was carbon fibres.[103] It was found that a suitable casting material for the fixation of the polymer specimens in the ultramicrotome holder is molten sulphur.[104] However, at present organic polymers are fixed with the aid of casting materials based on epoxide compositions and cryoultramicrotomes are used for the preparation of sections.[105,106] It is noteworthy that hitherto the method of EMD of sections has been used to investigate the local order in the specimen; there have been no publications on structural analysis using this technique.

Examination of the methods of preparation of polymer objects for microdiffraction studies shows that in many cases this procedure can introduce artefacts associated, for example, with the influence of the rate of evaporation of the solvent, random deformation, etc. These processes must be investigated in order to eliminate the artefacts and to make the results of the investigation more correct. On the other hand, phenomena of this kind are also studied specially in order to reveal a whole series of properties of polymers and in this respect electron microscopy has a considerable scope. Overall, the literature data show that there is no universal

method of preparation of polymer specimens. Each object requires an individual approach and considerable preparatory work in order to select the correct conditions and success depends in many respects on the skill of the experimenter.

The problem of protecting the polymer specimen from radiation during focussing and photography merits special attention not only from the standpoint of the reliability of the diffraction data but also from the standpoint of the very possibility of such an investigation. This is especially important when the goniometric method is used, where, in the course of the short lifetime of the crystal, it is necessary to rotate the specimen in order to obtain a three-dimensional diffraction pattern, as has been done, for example, in studies of compounds (V) and (XII)–(XVI) (see Table).

One of the causes of damage to the specimen by the electron beam is ionisation and excitation of atoms and molecules, as a consequence of which the initial equilibrium state of the substance breaks down. There are special publications on this question in the literature.[107] The mechanism of the effects of irradiation on organic objects has not been finally elucidated but it has been established in relation to polymers, for the maximum irradiation dose, which is specific to each polymer, that the specimen is fully converted into an amorphous form while the morphology of the supermolecular formations is retained.[79,108] The sensitivity of the polymer specimen to irradiation is associated with its chemical structure. In particular, as aromatic fragments accumulate in the macromolecule, the resistance to irradiation increases. Thus, it has been found that crystals of poly(*p*-xylylene) are fully converted into an amorphous form in an electron microscope with an accelerating potential of 500 kV for an overall irradiation dose exceeding by a factor of 20 that for polyethylene.[54] Polymers with a higher resistance to irradiation can be successfully investigated by the EMD method, but it has been shown by a number of workers that objects sensitive to irradiation are also susceptible to electron diffraction observations and special precautions are taken against damage [compounds (XII)–(XVI)—see Table].

The method of protecting the object is to reduce to the maximum extent the intensity of the electron beam and also to shorten the residence time of the specimen under irradiation, especially the exposure time. The procedures for the protection of the object against irradiation have been examined in extremely great detail by Dobb et al.,[109] who suggested that a special disc covering the central portion of the beam during the focussing of the image be inserted in the aperture holder of the second condenser. On the other hand, the exposure of the object to the electron beam entails the appearance of carbon contaminations, which reduce the information content of both the image and of the electron diffraction pattern as a result of the enhancement of the diffuse scattering background. The question of the nature of the contaminations and of the methods of dealing with this phenomenon is considered in special manuals[98] (p.25). Devices for cooling the object to the temperature of liquid nitrogen are constantly used in studies involving the measurement of reflection intensities for protection against irradiation [compounds (IX) to (XXI)—see Table]. Such devices are present in all modern microscopes.[1] The use of highly sensitive photographic emulsions plays an important role in diminishing the exposure time during photography. The latest transmission electron microscopes are fitted with devices which make it possible to reduce the period during which the electron beam acts on the specimen with the aid of two pairs of deflecting systems.[1] The use of high-voltage microscopes makes it possible to enhance the local nature of the diffraction and also to reduce the exposure time.

However, the problem of protecting the specimen against irradiation has been solved most radically with the aid of a new technique of diffraction studies developed towards the end of the 1970's, which consists in the joint use of transmission of and scanning with an electron beam having a small diameter.[110–112] Whereas in the usual TEM the size of the irradiated part of the object is determined by the diameter of the selective diaphragm located below the object holder and amounts to ~1 μm or more, in the scanning-transmitting EM the beam diameter is itself limited and the diffraction area, determined by the diameter of the probe, can be reduced to 300–100 Å. The new method used in the scanning-transmitting electron microscope permits an enhancement of the local nature of the diffraction, an increase of its resolution, and the maximum protection against irradiation of the parts of the object adjoining the test region, as has been demonstrated in a study of polyethylene.[110] An example of the use of this method for the study of crystal structures is provided by the investigation of poly(*p*-oxybenzoyl) (VIII) (see Table).

Overall, the results of modern studies on diffraction EM have shown that, although the problem of protecting the polymer against irradiation requires constant attention, nevertheless it is not an obstacle to the use of the given method in the structural analysis of high-molecular-weight compounds.

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The review of publications on the electron microscopy of polymers permits the conclusion that this method has advanced appreciably not only in connection with the development of high-resolution instruments but also as a consequence of the development of methods for the quantitative analysis of electron microdiffraction patterns. However, one must also conclude that the structural analysis of polymers with the aid of TEM has still not become a standard procedure. The reason for this is the inadequate availability of improved electron microscopes and also the difficulties in the preparation of the specimens and in the interpretation of electron microscope data. As regards the interpretation of visual high-resolution TEM images, it is useful to bear in mind the words of Kabayashi, the renowned specialist in this field, that to see in the electron microscope does not necessarily mean to believe.[113]

The determination of the crystal structures of polymers requires their combined study by means of several independent methods, among which electron microdiffraction plays an important role. The accumulation of experience concerning the application of EMD and the continuing improvement of the instrumental technique undoubtedly open up prospects for the development of electron microscopy up to a readily accessible standard method for the structural analysis of high-molecular-weight compounds.

During the preparation of the review for printing, a series of communications, both methodological and of a review character, concerning the use of electron microscopy for the structural investigation of polymers were published. Thus a method has been developed[114] for the epitaxial growth of polyethylene crystals in order to obtain and analyse EMD patterns. The same workers in another communication[115] analysed in detail the possibilities of the epitaxial method for the quantitative EMD analysis in comparison to crystallisation from solutions; the comparison was carried out in relation to a series of polymers, especially biological polymers.

Review data on the use of the EMD method in polymer chemistry have been included in the publication by Dorset.[116] The advances of electron microscopy in securing quantitative information about the structure and composition of polymers

have been described in a review[117] which deals with problems of the use of spectroscopic-analytical information and also with the protection of the test object against damage by irradiation. A novel microdiffraction method involving the shift of the aperature diaphragm, which replaces, in the authors' view, the goniometric technique, has been proposed.[118]

Data on the structure of poly(butylene terephthalate) and of its block copolymers have been obtained by the EMD method in the scanning-transmission mode.[119] The structure of poly(3-hydroxybutyrate) has been determined.[120] Studies by Japanese workers, using the entire range of the diffraction and visual possibilities of high-voltage TEM, have been continued—in particular, the structures of a conducting polymer, namely poly(1,4-phenylene),[121] and also of isotactic polystyrene[122] have been studied.

The results of the studies quoted above demonstrate the continuously increasing contribution of the microdiffraction electron microscope method to the crystal-chemical research into high-molecular-weight compounds.

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Nesmeyanov Institute of
Organoelemental Compounds,
USSR Academy of Sciences,
Moscow