Structure and morphology of poly(2,3-dichlorobutadiene)

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The X-ray diffraction, electron microscopy and electron diffraction studies of the structure and morphology of poly(2,3-dichlorobutadiene) confirmed the polymorphic character of this polymer. The structure of polymerized samples or samples crystallized from solution is monoclinic. By annealing the original monoclinic sample at temperatures above 140° C or by crystallizing from the melt, the orthorhombic crystal modification is formed. The variety of morphological structures found in solution-crystallized samples depends on the quality of the solvent or solvent–non-solvent system used.

INTRODUCTION

The data published on the structure and morphology of poly(2,3-dichlorobutadiene) (PDCB) are scarce. Brown and White[1] report that PDCB is highly crystalline, soluble and cannot be melted without decomposition. I.r. spectroscopy and X-ray diffraction confirmed the *trans*-1,4-poly(2,3-dichlorobutadiene) configuration. During heating the polymer turned brown at about 240°C and crosslinked. The samples with all *trans*-1,4 configuration crystallized from chlorobenzene and tetralin solution in the form of long needles. Chatani *et al.*[2,3] investigated the crystal structure of PDCB prepared by gamma irradiation of the canal complex of the 2,3-dichlorobutadiene and thiourea. The resulting polymer had a high content of the *trans*-1,4 configuration and crystallized in a monoclinic cell. By rolling of the monoclinic polymer a new orthorhombic crystalline modification was found.

In this work, we have examined the structure and morphology of PDCB samples prepared by solution and emulsion polymerization.

EXPERIMENTAL

Samples

The characteristics of the PDCB samples used in this work are summarized in *Table 4*. The preparation and characterization of the samples is described elsewhere[4]. From the i.r. spectra it was concluded that both emulsion and solution polymerized samples have mainly the *trans*-1,4 configuration and about 5% 1,2-units. The *cis*-1,4 configuration was not detected.

X-ray diffraction

X-ray diffraction was on a goniometer using quartz monochromatized CuKα radiation. Flat film photographs were taken with Ni-filtered CuKα radiation in an evacuated camera. For the measurement at higher temperatures an electrically heated sample holder was used.

Electron microscopy

Solution crystallized samples were prepared by dissolving 0.05% PDCB in a given solvent and cooling to the crystallization temperature T_c = 50°C and after 2h cooling down to room temperature. The crystal suspension was dropped on a carbon coated grid. After solvent evaporation the sample was shadowed by WO_3 or Au at 25°C. Free surface replication was done by means of poly(acrylic acid) and C. Electron diffraction was performed at 80 kV. Measurements of the Bragg spacings was calibrated by reference to Au, used for sample shadowing.

RESULTS AND DISCUSSION

The X-ray diffraction spectra of the as polymerized PDCB powder and solvent cast films were typical for the mono-

Table 1 PDCB sample characteristics

Sample	Polymerization					X-ray crystallinity (%)	$[\eta]^d$ (dl/g)
	Type	T, °C	Initiator (wt %)	Conversion (%)	Chain transfer agent, (%)		
E-1	Emulsion	20	0.02[a]	64.3	–	54.2	2.43
E-3	Emulsion	20	0.02[a]	63.9	5[c]	55.0	0.85
E-4	Emulsion	75	0.015[a]	47.1	–	51.5	2.20
R-13/4	In benzene	75	0.4[b]	71.5	–	70.5	0.73
R-15/4	In CCl_4	75	0.5[b]	99.2	–	65.5	0.69

[a] Na salt of the *p*-methylbenzene diazothioglycol acid; [b] benzoyl peroxide; [c] dodecyl mercaptan; [d] in toluene at 80°C

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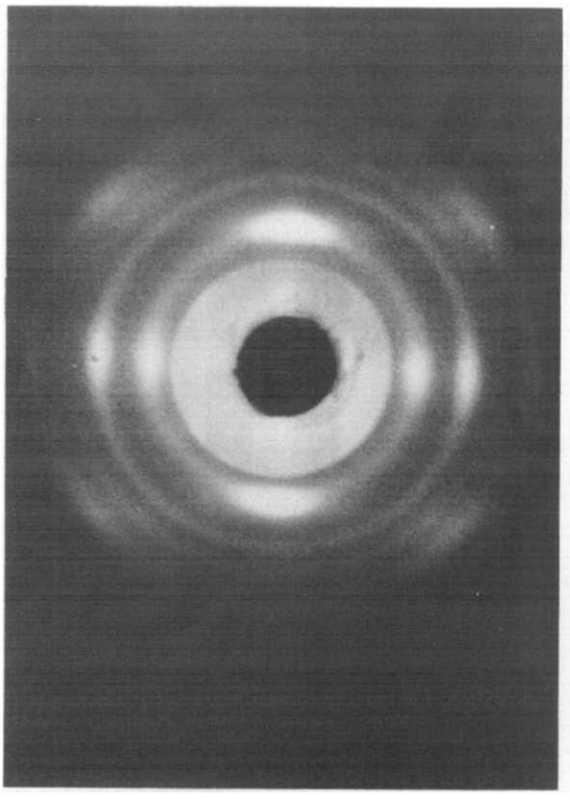

Figure 1 X-ray diffraction pattern of the R-13/4 sample cast from solution and uniaxially stretched at 100° C. Stretching direction vertical

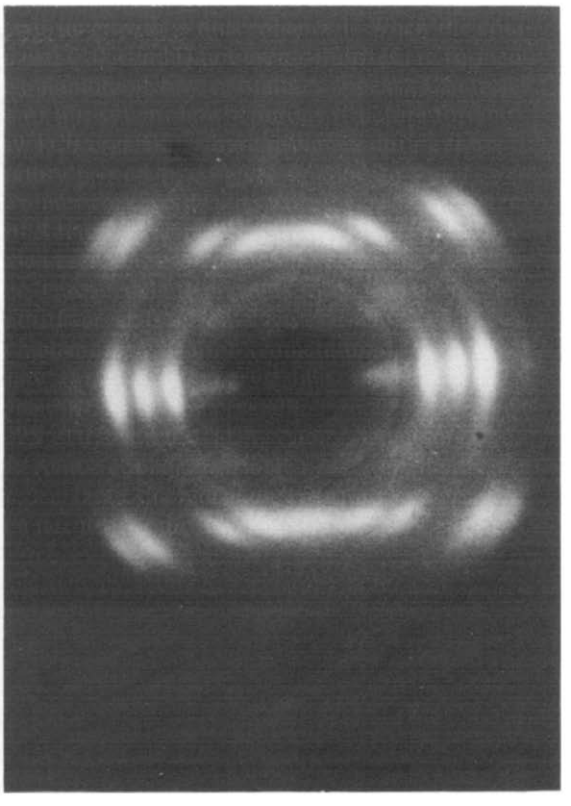

Figure 2 X-ray diffraction pattern of the R-13/4 sample pressed 3 min at 170° C and 25 MPa

clinic crystal structure described by Chatani *et al.*[2]. X-ray crystallinity of the solution polymerized samples was markedly higher than that of the emulsion polymerized ones. The crystallinity could be measured only at the original powder or solution cast PDCB samples, because the sheets pressed at higher temperatures and pressures were oriented and showed a phase change, as will be discussed later.

Stretching of the solvent cast or pressed samples at temperatures below 100°C leads to uniaxial orientation with the *c*-monoclinic axes (chain axes) oriented preferentially in the stretching direction. The low molecular and higher crystalline samples oriented most easily.

Annealing

Up to 135°C, the original monoclinic structure does not change substantially. With increasing annealing temperature the peak intensity decreases and an amorphous halo with the diffuse maximum at $d = 0.61$ nm is apparent. At 153°C, the melting of the monoclinic modification continues and there are visible orthorhombic reflections. At 166°C mainly the amorphous halo with few faint crystalline peaks could be seen. After cooling to 33°C many sharp diffraction peaks reappear which conform to the orthorhombic crystal modification of PDCB. The only exception to this is the peak having $d = 0.565$ nm which does not belong to any known crystal modification of PDCB. In considering these structural changes, one must bear in mind the low thermal stability of PDCB and its pronounced tendency to crosslink. In any case, it is apparent that the original monoclinic modification tends to recrystallize at temperatures between 120°C and the melting temperature to the more stable orthorhombic modifiation. Cooling the molten PDCB to room temperature also gives rise to the orthorhombic crystal structure.

Table 2 The morphology of dilute solution crystallized PDCB

Sample	Solvent / Non-solvent	Morphology
R-15/4	Cyclohexane	Complex lamellar formations, multilamellar flakes
E-1	Benzene	Grainy lamellar formations 0.5–1 μm
E-3	Amylacetate	Leaf-like multilamellar formations
R-15/4	Dioxane	Lamellar fringed dendrites and globules 0.2–0.4 μm
E-1	$C_2H_2Cl_4$	Grain structures (500 nm) connected into a network
R-15/4	Dimethylphthalate	Individual globules 0.2–0.7 μm
R-15/4	CCl_4 / Propanol	Defect lamellar formations, multilamellar flakes
E-1	Chlorobenzene / Amylacetate	Defect lamellar structures, fibre rows of the shish-kebab type
R-15/4	Xylene / Propanol	Fibrillar spherulites
R-15/4	C_2Cl_4 / Ethanol	Fibrillar spherulites
R-15/4	C_2HCl_3 / Ethanol	Crowd of lamellar globules 0.5–1.5 μm
R-15/4	Cyclohexane / Propanol	Fringed lamellar globules 1–2 μm

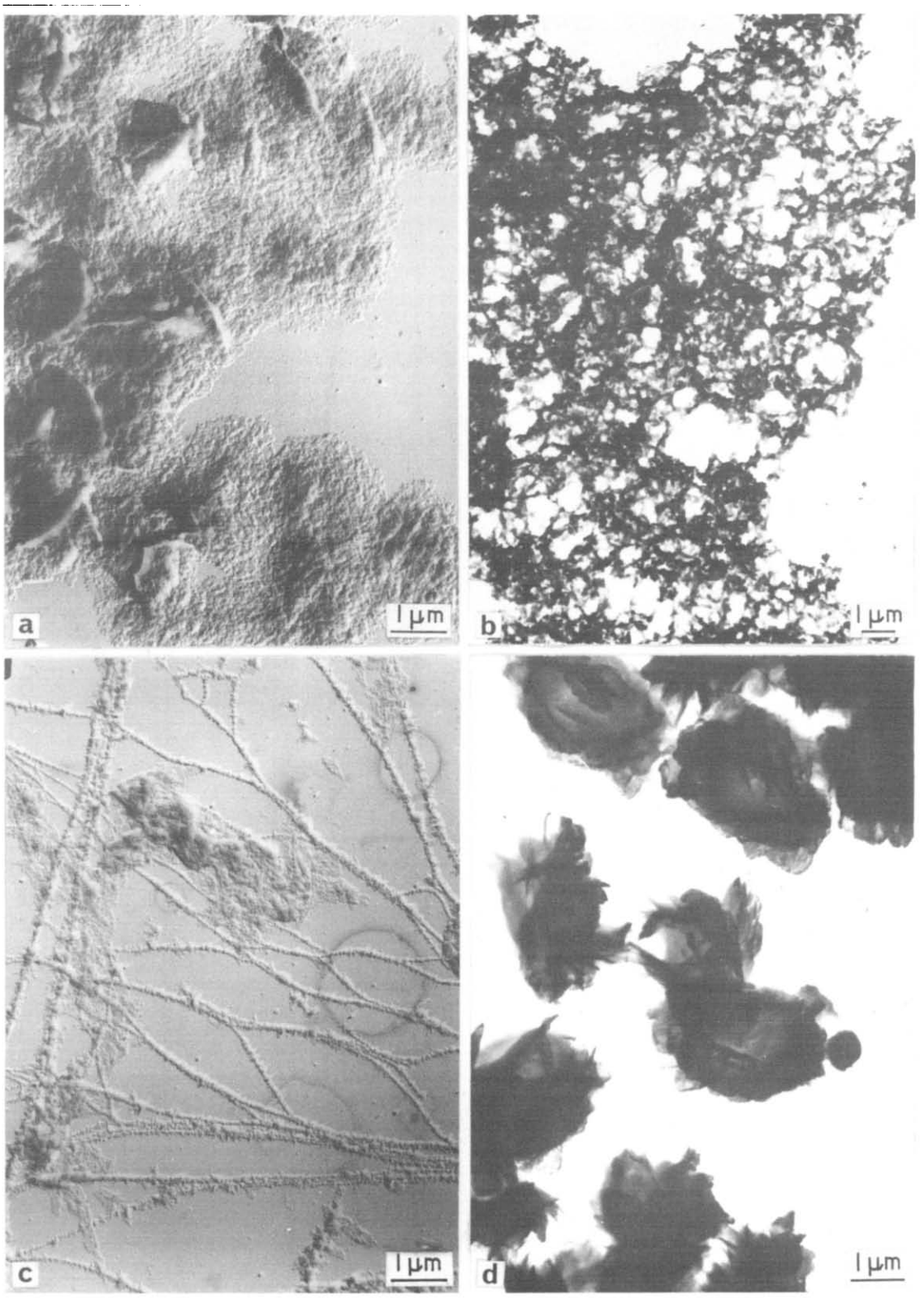

Figure 3 Electron micrographs of PDCB samples crystallized from dilute solution of: (a) cyclohexane; (b) tetrachloroethane; (c) chlorobenzene + amylacetate; (d) cyclohexane + propanol

Pressed samples

Sheets of PDCB prepared by pressing the monoclinic powder material at 10–25 MPa exhibit markedly oriented texture. Pressing at 100°–130°C leads to the oriented monoclinic structure (*Figure 1*), pressing at 135°–170°C to oriented mixed monoclinic and orthorhombic structure. Increasing the temperature resulted in a higher degree of orientation, but the phase change to the orthorhombic cell was never complete (*Figure 2*).

Solution crystallized samples

The morphology of the dilute solution crystallized samples from various solvents or solvent–non-solvent pairs is briefly characterized in *Table 2* and some typical micrographs are

shown in *Figure 3*. Depending on the solvent used practically all known morphological formations could be observed: simple lamellar systems, complex globular, lamellar–fibrillar and spherulitic morphologies. This is in full accord with our previous findings[5] that the morphology of the solution crystallized polymer depends on the solvent power of the solvent or solvent – non-solvent system used and on the sample molecular weight. In spite of using various solvents, solvent–non-solvent systems and various crystallization conditions, we did not succeed in preparing simple regularly shaped single crystals of PDCB. We suppose that this was due to the lower configuration regularity and branching of the samples used. Annealing of the solution crystallized samples has shown that the original lamellar structure such as in *Figure 3a* melts at 140°C and transforms at 160°C into dentritic lamellar spherulites (*Figure 4*). Above 200°C this new morphology melts again and an amorphous liquid like structure results.

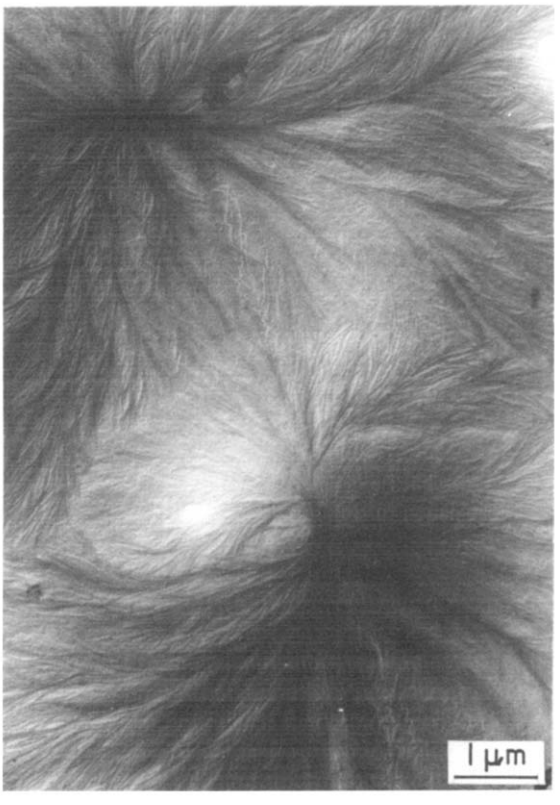

Figure 4 Electron micrograph of the R-13/4 sample crystallized from cyclohexane and annealed at 160°C

Electron diffraction

Selected area electron diffraction of most solution crystallized samples confirmed their polycrystalline nature characterized by few diffraction circles. The oriented diffraction arcs could only be observed in certain cases e.g with lamellar samples crystallized from cyclohexane (*Figure 5a*). Indexing of the diffraction spots agreed with the monoclinic crystalline cell. The orientation of the crystal cell in the lamellae was as follows: the *c* crystal axes were situated along the lamellar thickness and the *a* and *b* axes in the basal plane of the lamellae. It is clear than in lamellar PDCB crystals the chain folding occurs in the same way as it is with other crystalline polymers[6].

Investigation of the annealed samples revealed again that the morphology change is connected with the recrystallization. With increasing annealing temperature the arced diffraction peaks transformed to sharp diffraction spots (*Figure 5b*). This increase of crystallinity and orientation was connected with the phase transition of the monoclinic to the orthorhombic crystal cell having the parameters essentially equal to the values of Chatani *et al.*[3]. The phase transition

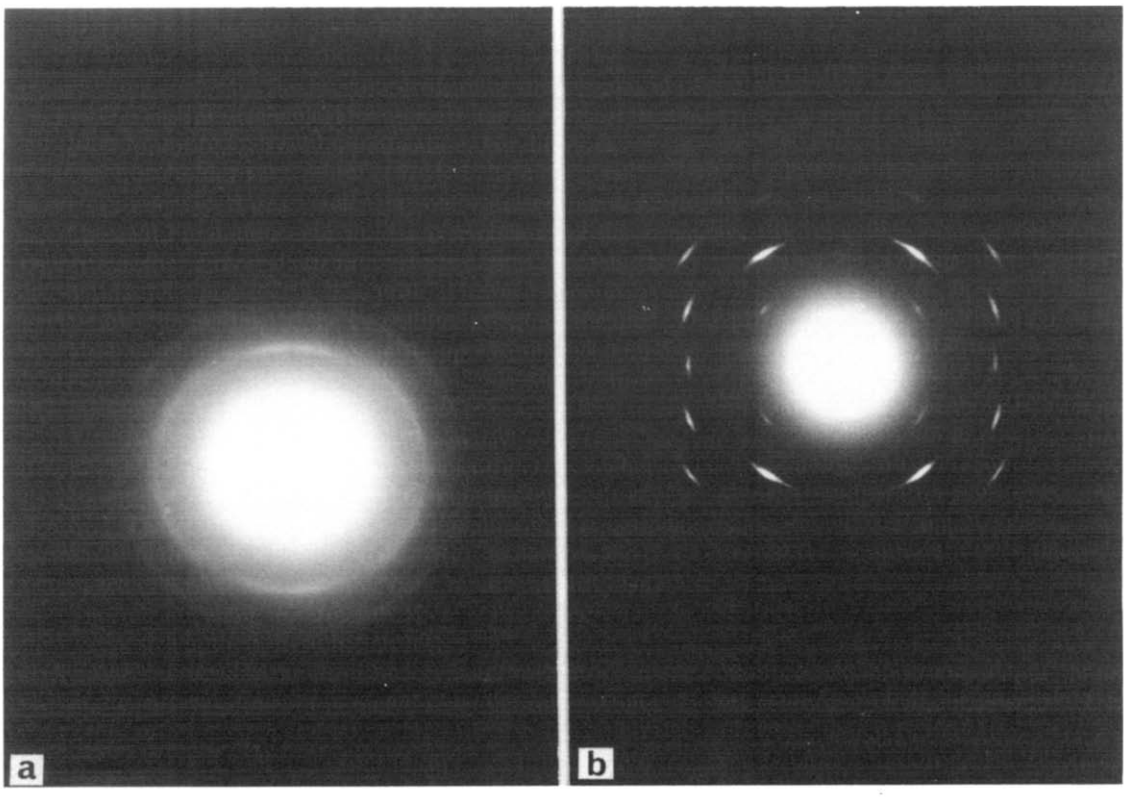

Figure 5 Electron diffraction pattern of PDCB samples: (a) crystallized from cyclohexane; (b) crystallized from cyclohexane and annealed at 180°C

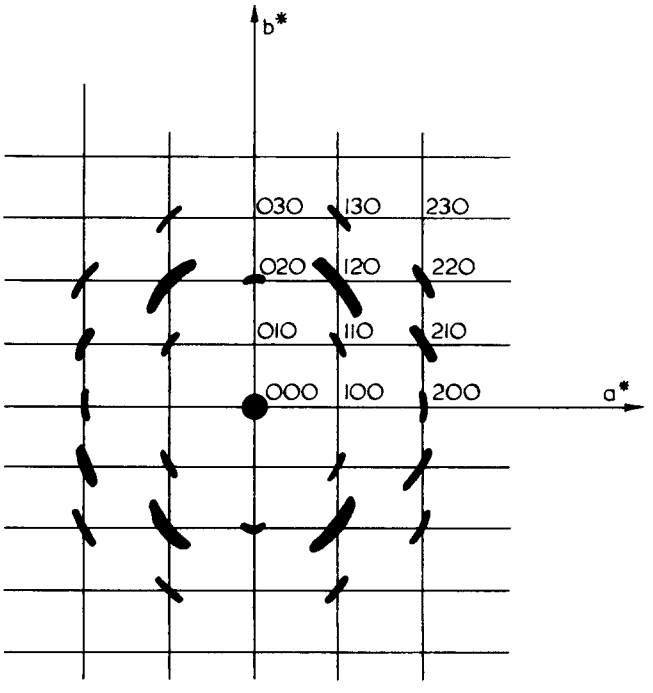

Figure 6 *a*b** projection of the PDCB reciprocal orthorhombic lattice and the observed electron diffraction spots from ***Figure 5b***

took place above 140°C. *Figure 6* shows the *a*b** projection of the PDCB orthorhombic reciprocal lattice with the electron diffraction spots observed with our samples. The *c* axes remain perpendicular to the basal plane of the lamellar crystal also in the orthorhombic cell.

Our experimental evidence shows that the orthorhombic crystal modification of PDCB is more stable than the monclinic one. The phase transition could be brought about simply by heating above 140°C without mechanical deformation.

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