spinodals are by definition confined to the temperature of those measurements.

We have also pointed out the possible pitfalls in such measurements in that manipulation of these data relies on invariance of the concentration fluctuations from sample to sample. This implies both good temperature equilibration and no effect of deuteration on the blend thermodynamics. This latter restriction is clearly a severe limitation since as discussed in the Introduction, many systems are already known to be affected. In a future paper we intend to tackle the problem of extracting interaction terms for a system where deuteration shifts the phase boundary (polystyrene with polybutadiene).

Finally, the data confirm that there is an extra (noncombinatorial) entropy of mixing for blends of PPGM with PEGM observed at low concentrations of PPGM and that this is favorable for mixing. Since no unusual conformational changes are observed for the PPGM molecules, this contribution may be associated with local conformational changes in the PEGM molecules.

Acknowledgment. We are grateful for the support of the scientific and technical staff at the Institut Laue-Langevin while carrying out these experiments. A.J.C. thanks SERC for support during the period of the work. Dr. Chai Zhikuan and Professor Shi Lianghe of the Chinese Academy of Science gave help with the initial experiments and Dr. M. Warner (SERC Rutherford) and Professor R. S. Stein (University of Massachusetts) have been involved in helpful discussion at the final stages of analysis.

Registry No. PEGM, 9004-74-4; PPGM, 37286-64-9; neutron, 12586-31-1.

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Notes

Poly(1,4-*trans*-cyclohexanediyldimethylene succinate): Electron Crystallographic Considerations

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Received December 19, 1983

Introduction

Electron diffraction data can be used qualitatively for structural analysis. However, it is vitally important that the intrinsic differences from X-ray diffraction be considered in order to extract a reliable structural model. Dorset has noted that the principal phenomena that affect the electron diffraction data from thin organic crystals are n-beam dynamical scattering[1] and crystal bending.[2] The separate consideration of these effects has been justified for thin crystal with small bend deformations for the test structures of a paraffin and a linear polymer.[3] If either of these effects is large, a kinematic structure analysis may give erroneous results.[4-6] A structural model is required in order to determine their importance in a particular case. There is consequently no alternative to the standard structural refinement initially.

The microcrystals used for electron diffraction are often deformed on the microscope grid, as evidenced by bend contours. On the basis of Cowley's model,[7] it may be shown that projections down a long crystallographic axis are most sensitive to bend effects, which may affect both the intensity data and the observed symmetry of the zone. The general effect is to reduce coherence in the electron beam direction so that the observed diffraction pattern may appear to come from only a part of the unit cell.

Dynamical scattering is a well-known phenomenon in electron diffraction where the scattering cross-section for electrons is much larger than for X-rays. Diffracted beam amplitudes may be calculated as a function of crystal thickness from a perfect crystal, using, for example, the Cowley–Moodie multislice technique. (For practical guidelines, see ref 8–10.) Each zone must be analyzed

0024-9297/84/2217-2202$01.50/0

Table I
Structure Factor Table after Analyses for n-Beam Dynamical Scattering Effects (*hk*0 Zone) and for Crystal Bending

	*hk*0 zone			*hkh* zone			*h,k,2h* zone		
hkl	$F_c{}^a$	F_o	$F_c{}^b$	*hkl*	F_o	$F_c{}^b$	*hkl*	F_o	$F_c{}^b$
020	79.3	80.1	77.6	020	79.7	82.3	020	79.8	78.7
040	3.5	20.0	3.1	040	19.9	2.8	040	20.0	2.2
060	4.4	9.9	6.0	060	10.0	6.9	060	10.0	5.6
080	1.7	5.0	4.1	080	5.0	5.1	080	5.0	3.7
110	144.3	140.1	144.0	101	19.9	22.7	112	24.9	25.0
120	35.0	31.6	37.1	111	24.9	23.7	122	17.3	14.1
130	20.0	22.4	8.5	121	3.5	7.5	132	8.7	4.6
140	13.1	15.8	13.6	131	14.0	6.1	142	5.0	4.7
150	4.6	7.1	5.9	141	14.0	14.0	152	7.1	5.0
160	1.0	3.5	2.6	151	7.1	3.5	162	10.0	7.9
200	61.2	64.9	58.9	161	7.1	4.2	182	7.1	5.5
210	15.0	19.4	20.6	181	5.0	5.0	1,10,2	3.5	2.8
220	23.3	22.3	22.6	1,10,1	5.0	5.1	204	24.5	23.4
230	25.1	21.3	28.2	202	12.2	11.2	214	13.2	15.3
240	3.6	4.5	6.9	212	19.3	22.9	224	14.1	16.9
250	4.0	5.0	2.7	222	15.7	18.4	234	10.0	15.7
310	11.9	14.1	14.2	232	7.1	5.8	244	5.0	5.5
320	8.6	11.2	11.6	242	8.7	5.3	254	16.7	17.8
330	3.6	6.1	10.1	252	3.5	4.2	264	10.0	13.8
340	5.1	6.1	10.0	262	8.7	4.5	274	8.7	6.9
				272	3.2	2.7	284	10.0	8.5
				292	8.7	7.4	316	14.1	19.7
				303	12.2	7.4	326	19.4	29.5
				313	11.2	11.8	336	27.4	26.9
				323	3.5	3.8	346	5.0	5.4
				333	3.5	5.3	356	12.2	9.3
				343	5.0	5.5	376	7.1	5.4
				353	7.1	8.7	408	10.0	9.9
				393	8.7	8.7			
				414	7.1	8.9			
				434	7.9	7.7			
				444	8.7	6.8			
				454	15.7	17.9			
				464	5.0	7.3			
				474	8.7	7.2			
				505	12.2	11.2			
				525	5.0	3.6			
				555	5.0	8.6			
projection length, Å		13.51			10.14			10.36	
B, Å^2	4.0	4.0			3.0			5.0	
bending, deg		2.0			2.0			3.0	
R	0.132	0.155			0.209			0.199	

[a] After analysis for n-beam dynamical scattering effects. [b] After analysis for crystal bending.

individually, as the intensity of a particular reflection will depend on dynamical interactions with the other excited beams.

In the present note the three zones of data from poly(1,4-*trans*-cyclohexanediyldimethylene succinate), hereinafter called poly(*t*-CDS), used in the electron structural determination of Brisse, Rêmillard, and Chanzy[11] are examined in order to determine the extent of crystal bending and dynamical scattering effects and consequently the validity of the proposed structure.

Analysis

With the inclusion of crystal bending, all three zones showed an improved agreement factor $R = \sum||F_o| - |F_c||/\sum|F_o|$. The out-of-zone reflections noted in film C[11] with indices (3*k*5) and (4*k*7) have not been considered. For each zone the overall temperature factor and amount of crystal bend were changed until a minimum in R was found. The data sets were normalized in such a manner that $\sum|F_o|^2 = \sum|F_c|^2$. All three cases gave consistent results with the minima occurring for about 2° of crystal bending with an overall temperature factor of $B = 4$ Å^2. In each zone the projection axis is quite long and the minimum is well characterized. The average improvement in agreement is 3% in R. Details are presented in Table I.

Dynamical structure amplitudes were compared with observed values over a range of crystal thicknesses. For the *hk*0 zone the minimum in R occurs at 54 Å although the experimental estimate is 100 Å. This type of discrepancy has previously been noted in the analysis of electron diffraction data from other linear polymers.[12] The agreement factor at 54-Å thickness is $R = 0.132$, indicating that dynamical scattering causes relatively small changes in the diffraction data and leads to improved agreement with the experiment. For the *hkh* and *h,k,2h* zones, in which the data appear less reliable, best agreement with experiment was obtained at one unit cell thickness and is within 1% of the kinematic values.

The change in structure amplitudes for reflections along the tilt axis was calculated, as the crystal is tilted about *b* to the various zones. There are only small changes in amplitudes in the three zones from a 100-Å-thick crystal, with the data sets normalized to take account of the different effective crystal thicknesses. They thus can be confidently used to scale the three data sets together, as in ref 11.

In the *hk*0 diffraction pattern,[11] weak reflections of the types *h*00, $h = 2n + 1$, and 0*k*0, $k = 2n + 1$, are apparent. These reflections are kinematically extinct in the designated space group $P2_1/n$. Moreover, these reflections are also dynamically extinct under the rules given by Gjonnes and Moodie.[13] They may, however, be observed under several conditions: a slight misalignment of the crystal, an imperfectly flat crystal, or if there is multiple incoherent scattering. Their presence is thus consistent with the $P2_1/n$ designation in this case.

Discussion

The two experimental difficulties encountered when recording three-dimensional electron diffraction patterns arise from the short life span of the radiation-sensitive polymeric crystals. The difficulties are, first, how quickly and accurately one orients a crystal so that one of the crystallographic axes is coincident with the tilt axis of the goniometer and, secondly, finding the proper tilt angle to have the diffraction spots of the zone of interest exactly in the recording plane. An examination of the electron diffraction patterns of the hkh and $h,k,2h$ zones of poly(*t*-CDS) (Figure 2a of ref 11) indicates that these experimental problems have not been perfectly resolved. In spite of the problems described above, the electron diffraction data from poly(*t*-CDS)[11] provide consistent results in each zone studied. The three different microcrystals appear to have each a slight bend of about 2°. The diffracted beam amplitudes from these very thin crystals are slightly affected by dynamical scattering, confirming that the kinematic structure analysis of Brisse, Rēmillard, and Chanzy[11] is appropriate.

Three-dimensional electron diffraction data can be obtained from radiation-sensitive organic microcrystals and reliable structure amplitudes deduced when radiation damage is minimized[11] and crystal morphology and diffraction conditions are taken into account. Their utility for structure analysis has been demonstrated.[11]

Acknowledgment. D. L. Dorset is thanked for helpful discussions. Financial support from the National Science Foundation through Grant DMR81-16318 is gratefully acknowledged.

Registry No. (*trans*-1,4-Cyclohexanedimethanol)·(succinic acid) (copolymer), 81381-36-4; poly(*trans*-1,4-cyclohexanediyldimethylene succinate) (SRU), 81381-32-0.

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Radical Reactivity and *Q*–*e* Values of Methyl α-(Trifluoromethyl)acrylate

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Introduction

Analogues of poly(methyl methacrylate) (PMMA) incorporating halogen atoms in the α-position or in the ester side group have recently attracted much attention as sensitive electron-beam positive resists. Ito et al. have reported that methyl α-(trifluoromethyl)acrylate (MTFMA) does not undergo radical homopolymerization but readily polymerizes by pyridine initiation due to the low electron density on the double bond.[1] Radical copolymerization of MTFMA (M_1) with MMA (M_2) has been analyzed and yielded the monomer reactivity ratios of $r_1 = 0$ and $r_2 = 2.36$. Giese et al. have directly measured the substituent effect on the rate of addition of alkyl radicals to polymerizable alkenes by the "mercury method" (Scheme I)[2] and found that the rate constant of the cyclohexyl radical addition experimentally determined, k_{rel} (relative to styrene), is correlated to the Alfrey–Price *Q*–*e* parameters[3] as expressed by the following equation.[4]

$$\log k_{\mathrm{rel}} - \log Q_j = 0.5 + 0.825e_j \qquad (1)$$

Here the subscript j denotes a jth monomer.

Now we report the relative rates of the alkyl radical addition to MTFMA as well as Q and e values of MTFMA determined by combination of the copolymerization analysis and the mercury method. The Q and e parameters cannot be determined from only the monomer reactivity ratios in this case because $r_1 = 0$.

Experimental Section

Materials. MTFMA was custom synthesized by Parish Chemicals according to the method previously described.[1] Copolymerization of MTFMA with MMA and determination of the monomer reactivity ratios have been previously reported.[1]

Reaction of MTFMA with Cyclohexylmercuric Chloride. To a solution of 2.33 g (7.3 mmol) of cyclohexylmercuric chloride (**1**) and 1.97 g (14.6 mmol) of MTFMA (**2**) in 50 mL of dichloromethane was added 700 mg (14.6 mmol) of $NaBH_4$ in 5 mL of water at 20 °C. After 30 min, the reaction mixture was dried over $MgSO_4$ and distilled at 115 °C (bath temperature)/12 mmHg to give 1.36 g (79%) of the product **3**: IR 1750 (C=O), 1040 cm^{-1} (C–F); ^{1}H NMR (300 MHz) δ 0.78–1.96 (m, 13 H, $C_6\mathit{H}_{11}C\mathit{H}_2$), 3.13–3.31 (m, 1 H, $C\mathit{H}CO_2CH_3$), 3.77 (s, 3 H, $CO_2C\mathit{H}_3$). Anal. Calcd for $C_{11}H_{17}F_3O_2$: C, 55.45; H, 7.19. Found: C, 55.27; H, 7.13.

Kinetics. To a mixture of 64 mg (0.20 mmol) of cyclohexylmercuric chloride (**1**) and at least a 10-fold excess of MTFMA (**2**) and acrylonitrile (AN) (**4**) in 10 mL of dichloromethane was added 10 mg (0.3 mmol) of $NaBH_4$ in 1 mL of water at 20 °C.

Results and Discussion

When generation of the cyclohexyl radical from $C_6H_{11}HgCl$ and $NaBH_4$ is carried out in the presence of MTFMA, the adduct radical $C_6H_{11}CH_2\dot{C}(CF_3)CO_2Me$ captures H to give the product **3** in almost quantitative yield (80–95%), as is the case with many other olefinic monomers.[5] This quantitative addition of the cyclohexyl radical to the β-carbon of the olefinic double bond warrants

0024-9297/84/2217-2204$01.50/0