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# Polymerization in mixed crystals

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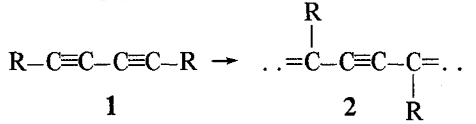
Suitably substituted diacetylenes can be co-crystallized to form substitutional solid solutions. By solid state polymerization of these mixed crystals macroscopic single crystals of statistical copolymers can be obtained. The co-crystallization is described and the influence of crystal composition on structure and reactivity in the solid state is discussed.

## 1. Introduction

1,4 substituted butadiynes (diacetylenes) are known to polymerize in the solid state. Due to the special mechanism of this topochemical polymerization,* macroscopic, nearly defect-free polymer single crystals can be obtained. The polymerization is initiated thermally or by irradiation. Each monomer joins with two neighbouring molecules in a 1,4 addition reaction to form a fully conjugated polymer chain according to Equation (i) [1]



$$\underset{1}{R-C\equiv C-C\equiv C-R} \rightarrow \underset{2}{..=\overset{R}{\overset{|}{C}}-C\equiv C-\underset{R}{\underset{|}{C}}=..}$$

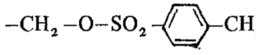
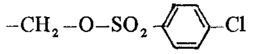
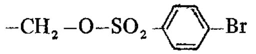
The polymer backbone formed is strictly linear and oriented along a well-defined crystallographic direction. Structures and physical properties of a large number of polydiacetylenes with different side groups have been determined [2]. According to the special polymerization mechanism copolymers can only be obtained if the comonomers form mixed crystals. These copolymer crystals are of interest because it can be expected that the polymer properties can be effectively varied by the copolymer composition. Similar effects in molecular crystals have been recently successfully demonstrated in the "isostructural doping" of charge-transfer crystals [3]. In addition, it should be noted that comonomer units introduced into the monomer lattice can be regarded as well-defined defect sites. These could be used as probes in order to obtain further inside into the complex process of energy transfer during the reaction and the nature of the reacting species which are not well understood to date.

The series of comonomers **1a**, **1b** and **1c** (see Table I) was chosen because the polymer **2a*** from 2,4-hexadiynylene di-*p*-toluenesulphonate (**1a**) is regarded in many respects as a model compound for polydiacetylenes. The monomer **1a** can be easily obtained in the form of large and perfect single crystals which can be polymerized under very mild conditions [1, 21]. In a previous communication [4] preliminary results of the formation and polymerization of mixed crystals of **1a** and **1b** was reported. In this paper a detailed investigation of co-crystallization, structural properties and polymerization behaviour of a series of diacetylenes forming mixed crystals is given.

## 2. Experimental details

2,4 Hexadiynylene di-*p*-toluenesulphonate (**1a**), 2,4 hexadiynylene di-*p*-chlorobenzenesulphonate

TABLE I The different crystal modifications chosen for this work

| 1,2 | R |
|---|---|
| a |  $-CH_2-O-SO_2-$ $-CH_3$ |
| b |  $-CH_2-O-SO_2-$ $-Cl$ |
| c |  $-CH_2-O-SO_2-$ $-Br$ |

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*Systematic IUPAC name: poly[1,2-bis(p-tolylsulphonyloxymethyl)-1-buten-3-ynylene].

(**1b**) and 2,4 hexadiynylene di-*p*-bromobenzenesulphonate (**1c**) were prepared by the method reported by Wegner [1]. Crystallization of mixed crystals was carried out by slow evaporation of acetone solutions of the monomers at 5° C. The different crystal modifications formed can be easily distinguished by their different crystal habit. The composition of the crystals was analysed by determination of the Cl and Br content [4–6]. Microcrystalline samples of the reactive modifications of **1b** and **1c** could be obtained by rapid crystallization from ethers like anisole or THF. These samples were always contaminated with crystals of the stable inactive modifications. Solid state polymerization was carried out by thermal annealing. The conversion was determined gravimetrically by extraction of residual monomer with acetone [1, 21]. At polymerization temperatures above 70° C the time conversion curves were obtained directly from the integration of the recording of an isothermal DSC scan [7–9]. Melting points of the reactive phases of **1b** and **1c** were determined with a microscope with a Kofler heating stage. Melting points of mixed crystals were determined by extrapolation of the melt peaks from DSC scans to zero heating rate.

For the determination of lattice constants crystals were mounted along the **b** and **c** crystal axes and double radius Weissenberg photographs ($R = 57.3$ mm) were taken. With monomer crystals the temperature was maintained at 120 K during the exposure to the X-ray beam by means of a low temperature attachment. At this temperature polymerization in the primary beam has been shown to be sufficiently slow in order to determine the data of the monomer [10, 11]. Microcrystals suitable for electron diffraction experiments were prepared by dropping solutions of the monomers in acetone on a water surface and by collecting the floating crystal films with carbon coated electron microscope grids.

## 3. Results and discussion

### 3.1. Formation of mixed crystals

A necessary and sufficient condition for the formation of substitutional solid solutions of organic molecules is similarity of the shapes and sizes of the component molecules. For the formation of a continuous series of solid solutions by two substances the structures of the pure components must be isomorphous [12]. Due to the rather irregular shape of organic molecules the principle of close packing [12] leads to structures of rather low symmetry so that the second requirement is not often fulfilled and only few systems of substitutional solid solutions of organic molecules have been well investigated. The monomers used in this investigation differ only by the substituent of the benzene ring so that it could be assumed that the first requirement of similarity of shape and molecular volume is fulfilled. However, the comonomers **1b** and **1c** crystallize in stable triclinic structures which are not isomorphous to the structure of **1a** [13].

In these structures the monomer packing is unfavourable for the polymerization and they are found to be completely unreactive in the solid state. By crystallization of these monomers at very high supersaturation from solutions in ethers, however, crystals of metastable reactive modifications can be obtained. Crystal habit and reactivity of these crystals resemble those of the pure **1a**. Unfortunately, the crystallization conditions necessary to produce these active modifications lead only to the formation of microcrystals. Microscopic pictures of the three active modifications are shown in Fig. 1. Under all crystallization techniques used so far the inactive forms of **1b** and **1c** seemed to be much favoured so that the microcrystalline samples obtained are always contaminated with varying amounts of inactive crystals. This difference of stability of the active and inactive phases can be understood by the large differences of melting points which are given in Table I. It should be noted that the metastable reactive crystals melt up to 50 degrees below the stable crystal forms. From the melt rapid crystallization of the inactive modifications is observed. Size and quality of the active crystals of **1b** and **1c** presently available do not allow X-ray diffraction experiments. However, electron diffraction patterns obtained from microcrystals indicate that we deal here indeed with isomorphous crystal structures (Fig. 2).

When **1a** is co-crystallized with **1b** or **1c** from organic solvents two sorts of mixed crystals are

TABLE II Melting points (° C) of the different crystal modifications

| | Active form | Inactive form |
|---|---|---|
| **1a** | 96 | –* |
| **1b** | 85 | 124 |
| **1c** | 99 | 148 |

*For **1a** no inactive crystal form is known

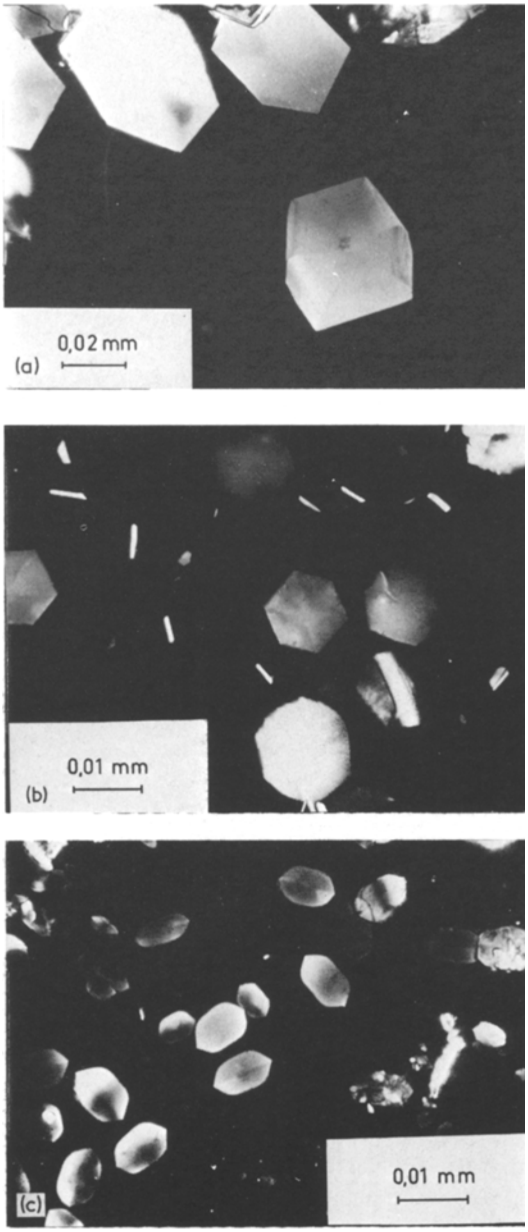


*Figure 1* Microscopic views of the reactive crystal modifications obtained under similar conditions by rapid crystallization from THF solutions. (a) **1a**, (b) **1b**, (c) **1c**.

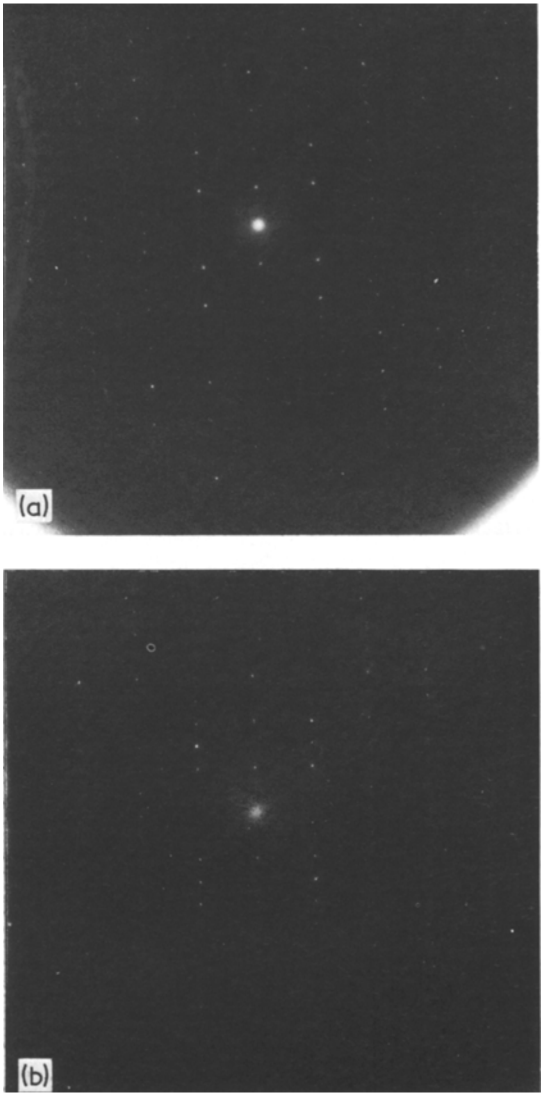
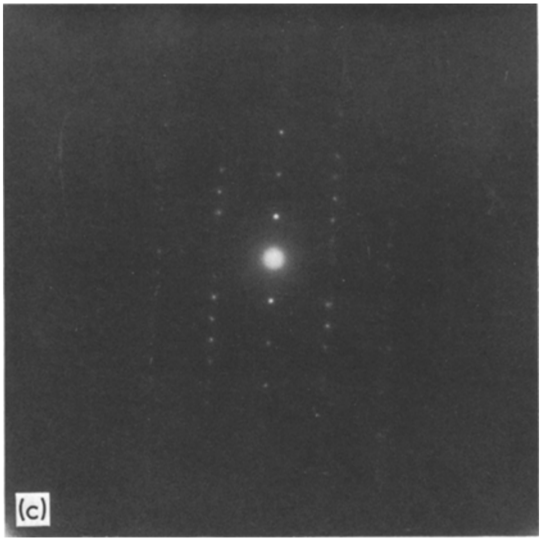


*Figure 2* Electron diffraction patterns of the reactive crystals. The $0\,k\,l$ reciprocal lattice plane is shown. (a) **1a**, (b) **1b**, (c) **1c**.

formed. The relative amounts and composition of the reactive and inactive phases depend on the composition of the crystallizing solution. The dependence of crystal composition on the relative concentration of the comonomers is shown in Fig. 3 and Fig. 4. The crystal composition curves for the active phases show a saturation behaviour whereas the inactive mixed crystals approach the limiting case of ideal solid solutions. It should be noted that the composition of the feed solution changes during the crystallization so that a certain variation of composition of the crystals should be observed. This variation is quite small, however, as the analysis of the composition of crystals which have been nucleated at different stages of the crystallization process shows. Up to 20 per cent of **1b** can be incorporated into the structure of **1a** without any changes of crystal habit and appearance. According to the large volume of the Br group the maximum amount of **1c** in mixed crystals is much lower. At high concentrations of the comonomers both the amount of reactive



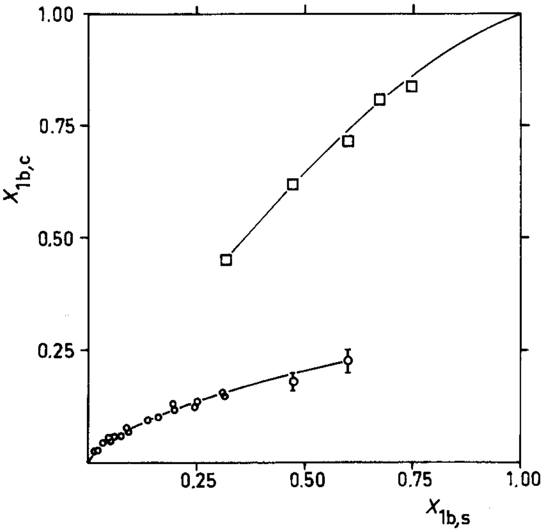


*Figure 3* Dependence of mixed crystal composition on the composition of the acetone feed solution. $x_{1b,s}$, $x_{1b,c}$: mole fractions of **1b** in acetone and crystal, respectively. ○: active modification, □: inactive modification.

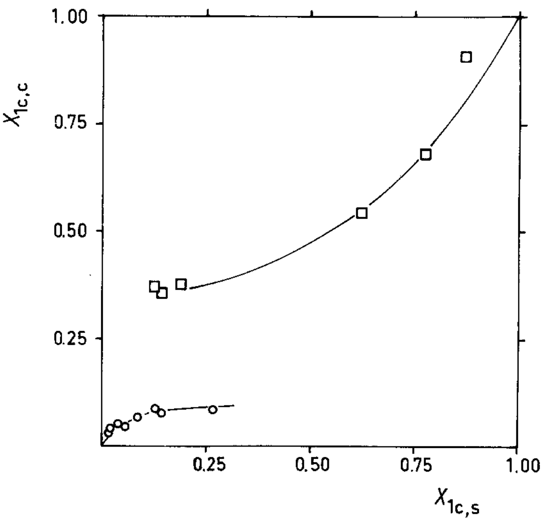
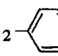
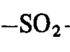


*Figure 4* Dependence of mixed crystal composition on the composition of the acetone feed solution. $x_{1c,s}$, $x_{1c,c}$: mole fractions of **1c** in acetone and crystal, respectively. ○: active modification, □: inactive modification.

material and size of the active crystals decrease. Apparently the phase diagrams of the investigated systems are quite complicated and have not been determined in detail. It should be noted that in our laboratory other systems of diacetylene monomers have been prepared which exhibit unlimited solubility of the components [6, 22]. Preparation of unsymmetrically substituted monomers (e.g. $R = -CH_2-O-SO_2-$$-CH_3$, $R' = -CH_2-O-SO_2-$$-Cl$) with the aim to widen the solubility range is in progress.

## 3.2. Structural investigations

Crystal structures of **1a** and **2a** are well characterized and have been used to demonstrate the dominating influence of monomer packing on the solid state reactivity of diacetylenes [11, 14, 15]. Projections of the monomer and polymer crystal structures on a common plane are shown in Fig. 5. The packing of diacetylenes can be described by the stacking distance of neighbouring monomers and by the angle which the diacetylene group makes with the stacking axis. Optimum reactivity is expected when the monomers stack in a distance equal to the polymer repeat unit of 4.9 Å with an angle near 45 degrees. In this case polymerization proceeds with minimum deformation of the monomer crystal by the growing chains. The polymer formed in a polymerizing diacetylene crystal is distributed statistically in the monomer matrix forming a solid solution. Although this simple geometrical approach is not able to explain all details of diacetylene polymerization it has been successfully used to explain qualitatively differences of reactivity between different monomers and crystal modifications [16]. It is interesting to note that introduction of comonomer units into the crystal of **1a** causes very little lattice deformation. The

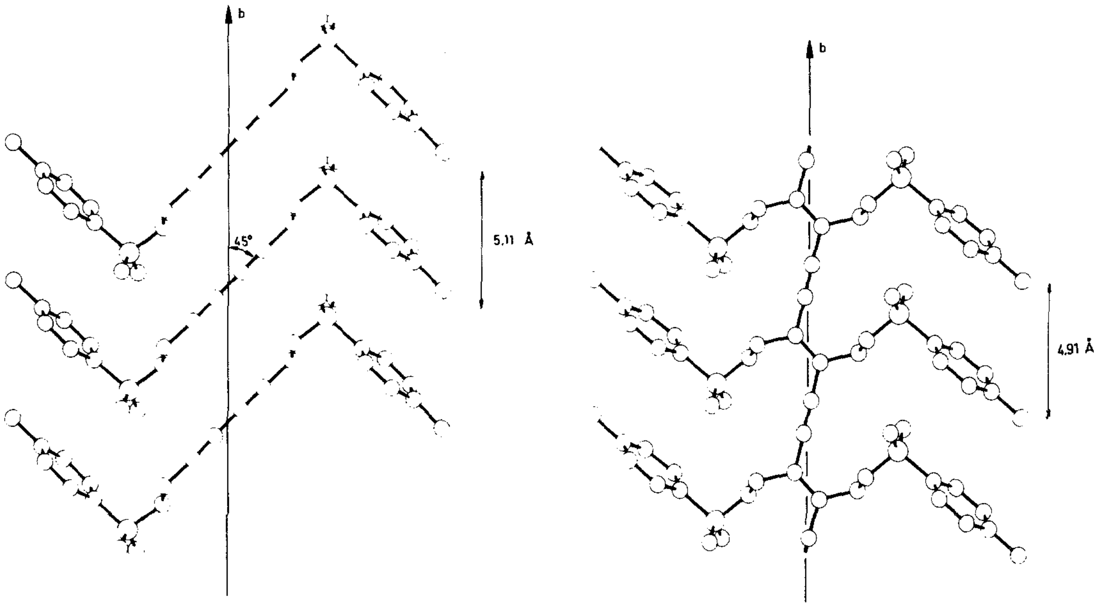


*Figure 5* Projections of the crystal structure of the monomer **1a** (left) and the polymer **2a** (right) on the plane of the polymer backbone.

only significant change that could be observed is a small and monotonic decrease of the stacking distance **b** which is shown in Fig. 6. Within the experimental error the other lattice parameters which reflect the lateral packing of monomer stacks do not change at all.

After polymerization only small increases of the length of the repeat unit could be detected. This result indicates that the packing of the phenyl rings in the side groups is perturbed by the bulkier substituents in the mixed crystals. Accordingly, the low temperature phase change which has been observed in pure **1a** and **2a** [11, 15, 17–19] is shifted to substantially lower temperatures [20]. This phase change of higher order has been shown to be a rearrangement of the side group packing with no detectable changes in the region of the diacetylene backbone. The property of the comonomer units to act as local defects of the side chain packing is also indicated by a gradual decrease of the intensity of the higher

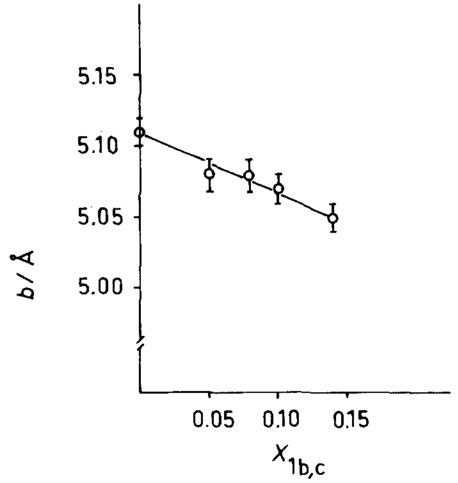


*Figure 6* Dependence of the monomer stacking axis **b** at 120 K on the mole fraction of **1b** in mixed crystal $x_{\mathrm{1b,c}}$.

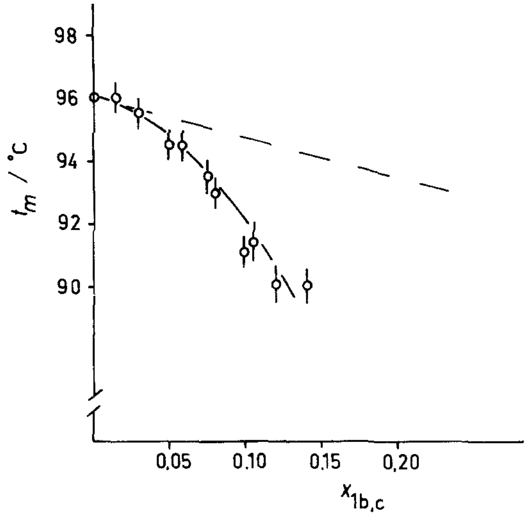


*Figure 7* Dependence of melting point of mixed crystals on the mole fraction of **1b**$x_{\mathrm{1b,c}}$; the dashed line represents the behaviour expected for ideal solid solutions.

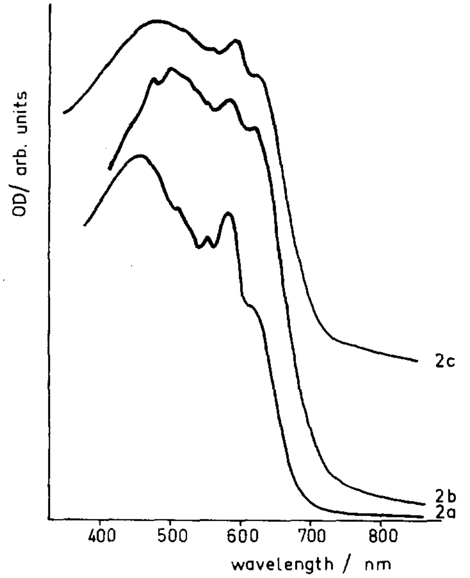


*Figure 8* Reflection spectra of the polymers **2a**, **2b** and **2c** obtained by thermal polymerization.

vibronic side bands of the polymer spectra. The dependence of the melting points of mixed crystals on the crystal composition is shown in Fig. 7. At concentrations of **1b** exceeding 3 per cent deviations from the behaviour expected for ideal solid solutions are observed.

## 3.3. Polymerization of mixed crystals

Since the reactive phases of **1b** and **1c** cannot be isolated in large amounts and in pure form their polymerization behaviour was only followed qualitatively. When **1b** and **1c** were polymerized thermally or by u.v. radiation no significant differences to the polymerization of similar samples of **1a** could be detected. Except for some differences in the fine structure of vibrational side bands the pure polymers obtained by thermal polymerization exhibit virtually identical optical spectra. Reflection spectra of **2a**, **2b** and **2c** are shown in Fig. 8. They are characterized by a sharp absorption edge caused by the conjugated polymer backbone at 650 nm.

The thermal polymerization of **1a** has been well investigated [1, 7–9, 11, 21]. It is characterized by a long induction period which at a conversion of approximately ten per cent is followed by a rapid reaction. Both the slow and the fast reaction have been shown to be of first order with identical thermal activation energies [7–9]. At present a complete mechanistic explanation for this behaviour cannot be given although it seems that changes of the lattice parameters and in particular the monomer stacking distance in the course of the reaction play an important role in the polymerization kinetics [11, 21]. It has been recently demonstrated that the reaction rate in the slow period can be varied a great deal by isotope labelling especially of the $-CH_2$ group, probably by changing the lifetime of the reacting species [9].

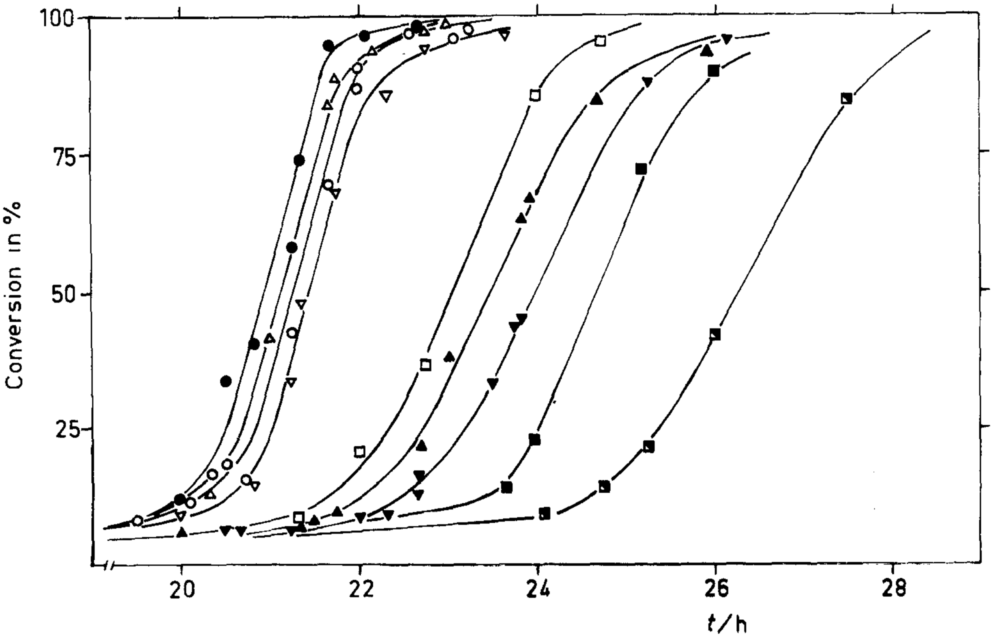


*Figure 9* Time conversion curves for the polymerization of mixed crystals at 60° C. ○: pure **1a**, △: $x_{1b} = 0.03$, ●: $x_{1b} = 0.05$, ▽: $x_{1b} = 0.06$, □: $x_{1b} = 0.08$, ▲: $x_{1b} = 0.10$, ▼: $x_{1b} = 0.11$, ■: $x_{1b} = 0.12$, □: $x_{1b} = 0.13$.

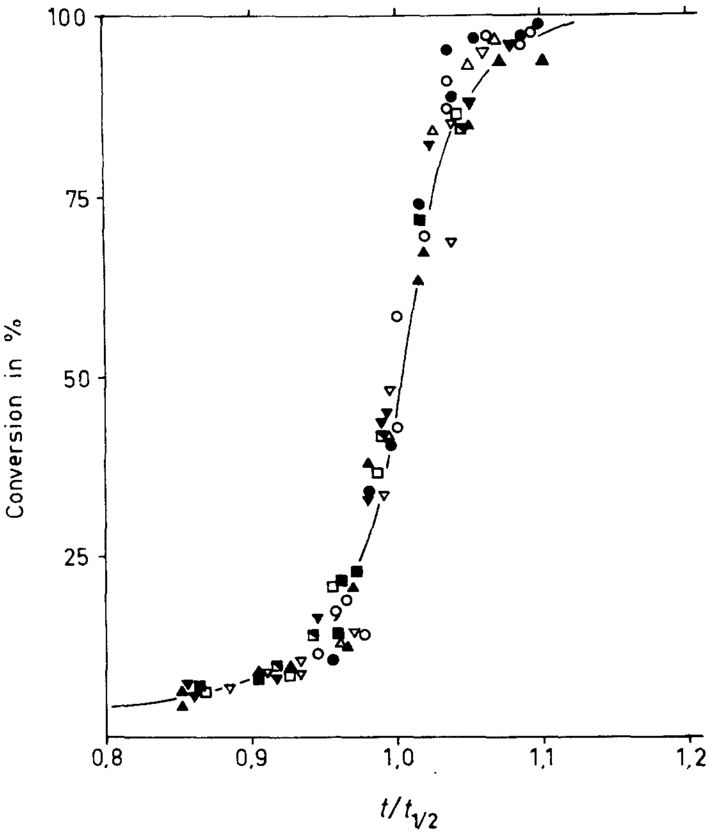


*Figure 10* Normalization of the time conversion curves shown in Fig. 9 to a common time scale.

The time conversion curves for the thermal polymerization at 60° C for a series of mixed **1a** and **1b** are shown in Fig. 9. The length of the induction period can be effectively varied by the crystal composition. It is interesting to note that at low doping levels below five per cent a small but significant increase in reactivity is observed. At higher comonomer contents the induction period is substantially increased. Within the experimental error the thermal activation energy of the thermal polymerization of mixed crystals of all compositions available are identical to the value of 91.5 ± 5 kJ $\mathrm{mol}^{-1}$ which has been determined for pure **1a** [7–9, 21].

The initial increase of reactivity at low comonomer concentrations cannot be understood on the basis of the simple geometrical packing model discussed above. Assuming a constant packing distance of the aromatic side groups the observed decrease of the stacking distance with increasing comonomer content leads to a continuous increase of the distance between the reacting atoms C1 and C4′. Consequently a decrease of reactivity is expected. It is possible that we deal here with similar effects as have been recently found with deuterated or $^{13}$C labelled **1a**. Here it is believed that the lifetime of the reacting species is changed without any changes of the monomer crystal structure [9]. When the time scale is adjusted by normalization to the time $t_{1/2}$ where fifty per cent conversion is reached the conversion curves for all compositions fall on one common curve (Fig. 10).

This treatment of the kinetic data has also been used for the polymerization of **1a** at different temperatures [7]. It should be mentioned, however, that the $t_{1/2}$ values are not characteristic times in the sense that they are related to the reaction mechanism which in all details is not well understood to date. Variations of reactivity can be reasonably well monitored using $t_{1/2}$ or the induction times. The activation energies which can be determined from Arrhenius plots using $t_{1/2}$, the induction times or the rate constants of the first order reactions are identical within the experimental error, although it should be emphasized that reasonable frequency factors can only be obtained using the first-order rate constants [8, 9]. Time conversion curves for a series of mixed crystals of **1a** and **1c** are shown in Fig. 11. Here the effect of isostructural doping on the reaction kinetics is less pronounced. At low

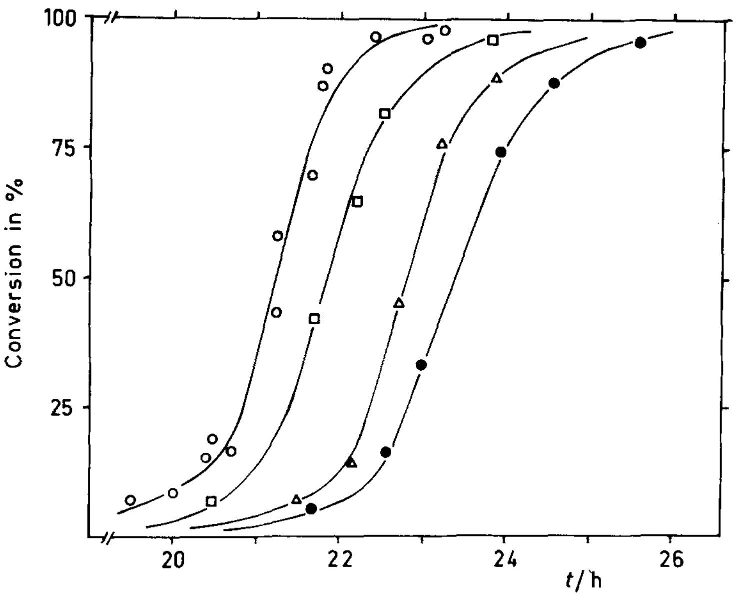


*Figure 11* Time conversion curves for the polymerization of mixed crystals at 60° C. ○: pure **1a**, □: $x_{1c} \doteq 0.028$, △: $x_{1c} \doteq 0.048$, ●: $x_{1c} \doteq 0.066$.

comonomer contents the induction period at 60° C remains constant and eventually increases in a manner similar to the other mixed crystal system. According to the larger volume of the Br groups less **1c** can be incorporated into the active crystals and so that the available concentration range is reduced. The question how the comonomer units are distributed in the monomer matrix and consequently about the copolymer statistics cannot be answered completely on the basis of the experimental data presently available. However, the following observations indicate that we deal here with a statistical distribution. Regardless of crystal composition no phase separation was detected and always complete conversion to polymer could be reached. Analyses of the residual monomer which can be extracted from partially polymerized crystals show that the composition of the residual monomer mixture and of the copolymer formed is always equal to the composition of the original monomer crystal. At the highest concentration levels of **1b** near twenty per cent no soluble oligomer fractions were obtained which should be observed if the comonomer acts as a site where the reaction is preferentially terminated.

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