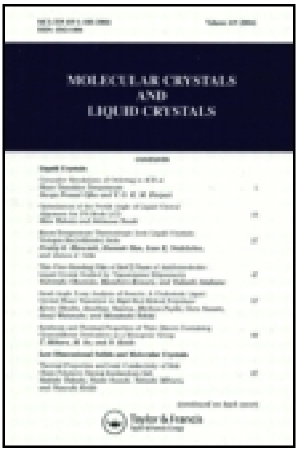

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrical and Dielectric Properties of Polymerizing Mixed Single Crystals of Diacetylenes: pTS-pFBS System

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Version of record first published: 24 Sep 2006.

To cite this article: Juliusz Sworakowski & Maciej E. Orczyk (1993): Electrical and Dielectric Properties of Polymerizing Mixed Single Crystals of Diacetylenes: pTS-pFBS System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 230:1, 71-76

To link to this article: http://dx.doi.org/10.1080/10587259308032215

Mol. Cryst. Liq. Cryst. 1993, Vol. 230, pp. 71–76
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Printed in the United States of America

ELECTRICAL AND DIELECTRIC PROPERTIES OF POLYMERIZING MIXED SINGLE CRYSTALS OF DIACETYLENES: pTS – pFBS SYSTEM

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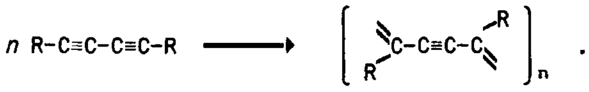
Abstract The paper presents results of measurements of evolution of the photoconductivity and the low-frequency electric permittivity of the mixed pTS-pFBS diacetylene single crystals during the thermally driven solid-state polymerization. The kinetics of the polymerization was found to be a function of the composition of the crystals, the rate constants in the induction and autocatalytic periods following different composition dependences. Changes in the kinetics of the photocurrent build-up essentially follow the changes in the polymerization kinetics. Temperatures of the phase transitions in the mixed crystals decrease with increasing concentration of pFBS, probably due to weaker dipole-dipole interactions between fluorobenzenesulfonyl side groups.

INTRODUCTION

Single-crystalline polydiacetylenes are a unique class of solids consisting of extended conjugated π-electron chains, 10^2–10^4 monomer units long, well separated from and relatively weakly interacting with one another. Since the pioneering work of Wegner,[1] structural, mechanical and electronic properties of this class of polymers have been extensively studied (see, e.g., Refs. 2-6 for reviews and collections of papers). The polymer single crystals are usually obtained by the solid-state polymerization of respective monomer crystals:



It should be noted that the polymerization results in *qualitative* changes of interactions modifying properties of the crystals: the monomers are in all respects typical molecular crystals, exhibiting a moderate anisotropy of their physical properties, whereas fully polymerized polydiacetylenes may be considered model one dimensional solids.

In some diacetylenes, such as pTS (R = $-CH_2-OSO_2-\Phi-CH_3$), the polymer chains formed at early stages of the polymerization are embedded in the monomer matrix, forming solid monomer - polymer solutions. Therefore, it seemed interesting to study evolution of properties of the system during the polymerization, and in particular the effect of the connectivity of the conjugated π-electron system on the electronic properties.

In our earlier papers, we reported on changes of the dielectric properties,[7-9] and on the photoconductivity build-up[10] of pTS single crystals during their thermal polymerization. Polymer content and temperature were found to influence the ε_2 component of the electric permittivity tensor, allowing one to follow both the polymerization kinetics and variation of the temperature of phase transitions. It was also shown that the photocurrent dependence on the polymer content is primarily a function of the probability of inter-chain jumps, the anisotropy of the photocurrent reflecting mainly the anisotropy of the main free path of charge carriers.

The present paper puts forward results of similar measurements carried out on mixed pTS-pFBS single crystals (in the latter diacetylene, R = $-CH_2-OSO_2-\Phi-F$). pFBS is isomorphous with pTS[11-13] and forms a series of solid solutions over the entire composition range.[14] The polymerization of pFBS is, however, much slower; moreover, both monomer and polymer pTS crystals exhibit well documented phase transitions (e.g., Refs. 15,16), whereas no signature of any phase transition has been observed in pFBS.[17]

EXPERIMENTAL

Mixed pTS-pFBS crystals were grown from acetone solutions by a slow evaporation at ca. 277 K, essentially as described in Ref. 18. The procedure of growth, handling, and determination of the composition of mixed crystals was described in more detail elsewhere.[7,10,19]

Most experiments described in this work were carried out on samples cut in such a way that the electric field was applied parallel to the direction of growing polymer chains (parallel to the crystallographic b direction); in some cases, the experiments were carried out on as-grown samples, with the field perpendicular to the chains. The polymerization was carried out *in situ*, at 333K.

The electric permittivities were determined from the capacitance measurements performed at 1 kHz. Polymerization-dependent photo-response of the samples was measured employing a typical time-of-flight setup[20], using a weak pulse illumination.

RESULTS

As was demonstrated earlier,[7,8] the ε_2 component of the electric permittivity tensor exhibits an anomaly around the temperature of the phase transition in pTS. Far from the transition temperature, ε_2 was found a nearly linear function of the polymer contents. The latter feature allowed us to monitor the kinetics of the solid-state polymerization of mixed crystals, their compositions covering the entire range from pure pTS to pure pFBS. Fig. 1 shows the conversion curves measured at 333 K for several mixed crystals. Both in the induction and autocatalytic periods, the conversion curves were found to follow the

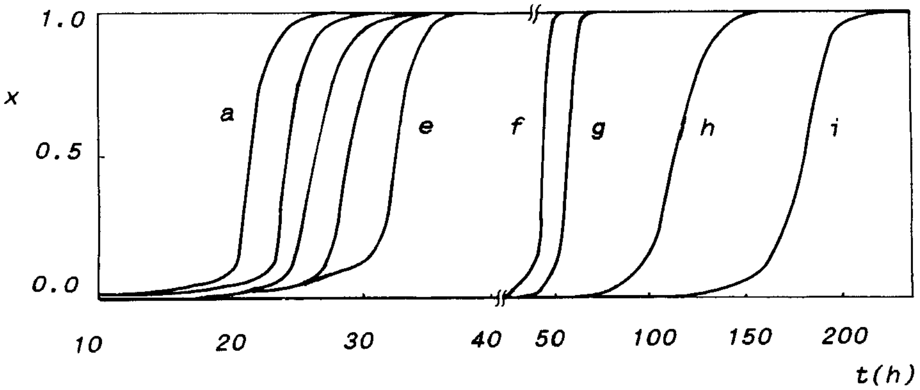


FIGURE 1 Monomer-to-polymer conversion curves measured during the thermal polymerization of mixed pTS-pFBS crystals at 333 K. The curves *a* through *i* refer to the following compositions of the samples (expressed in mole % of pFBS): 0, 5, 10, 15, 20, 28, 39, 54, and 100. Note the change of the time scale.

first-order kinetics, the rate constants being of the order of $10^{-6}s^{-1}$ in the induction period (k_i), and 10^{-5}- $10^{-4}s^{-1}$ in the autocatalytic period (k_a), in a good agreement with available literature data. It is interesting to note that k_i and k_a follow different composition dependences: k_a decreases monotonically with increasing mole fraction of pFBS (y), whereas k_i exhibits a maximum around $y \approx 0.5$.

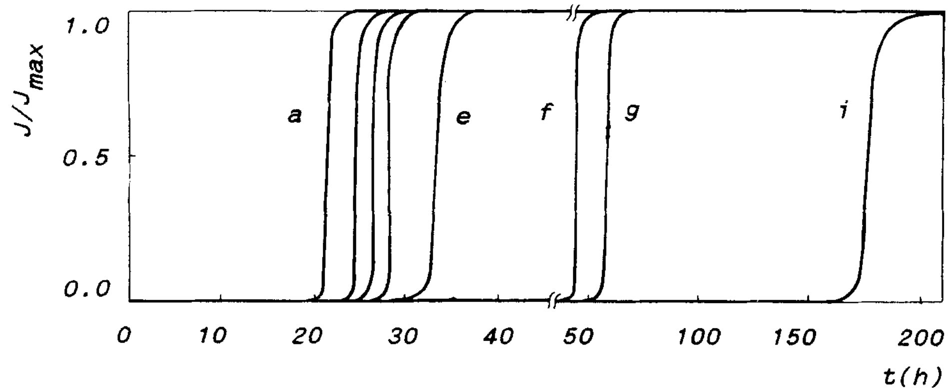
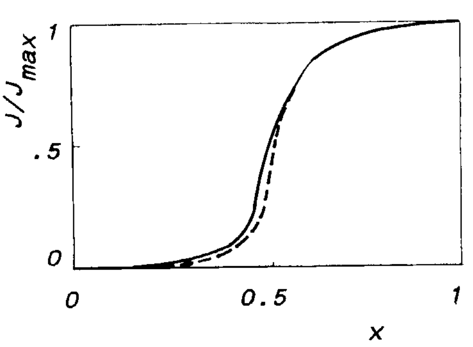


FIGURE 2 Photoconductivity build-up in mixed pTS-pFBS crystals during the solid-state polymerization at 333 K. The sample compositions are identical as in Fig. 1.

The evolution of the photoconductivity measured during the thermal polymerization of mixed pTS - pFBS crystals is shown in Fig. 2. The results, re-plotted on a common master plot (Fig. 3) show that the photoconductivity build-up in mixed crystals follows essentially the same dependence as that found previously in pure pTS.[10] However, we found the anisotropy of the photoconductivity in fully polymerized samples decrease monotonically with increasing y (cf. Fig. 4). Basing on the arguments raised in our earlier papers,[10] one may assume that the average unperturbed chain length in our samples is a decreasing function of y.

As was shown earlier,[7,8] measurements of the electric permittivity allow one to monitor the phase transitions in pTS at all stages of polymerization. The same technique was applied to the pTS-pFBS mixed crystals. The results, shown in Fig. 5, demonstrate that the transitions in both monomer and polymer shift towards lower temperatures. This shift



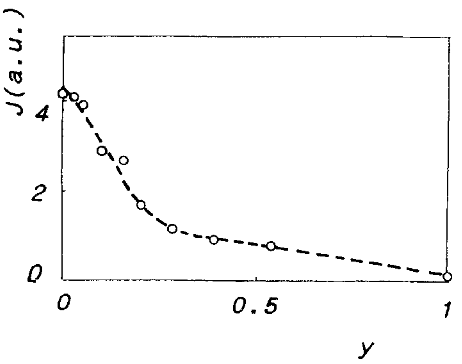


FIGURE 3 Photo-response in the pTS-pFBS in function of the polymer contents. Full line: pure pTS ($y = 0$), broken line: pure pFBS ($y = 1$). To within experimental error, data for all mixed crystals fall between the two lines drawn in the figure.

FIGURE 4 The photocurrent in mixed crystals, measured in fully polymerized samples at 333 K under identical illumination conditions and electric field, in function of the pFBS content. The illumination and the field were parallel to the direction the the polymer chains (b)

may be explained taking into consideration the fact that the transition in pTS involves ordering of highly polar *p*-tosyl side groups. A random substitution of these groups by the less polar *p*-fluorobenzenesulfonyl ones results in a decrease of the dipole-dipole interaction energy, and hence in a stabilization of the disordered phase. A simple model, put forward in Ref. 9, satisfactorily explains the behaviour of the system.

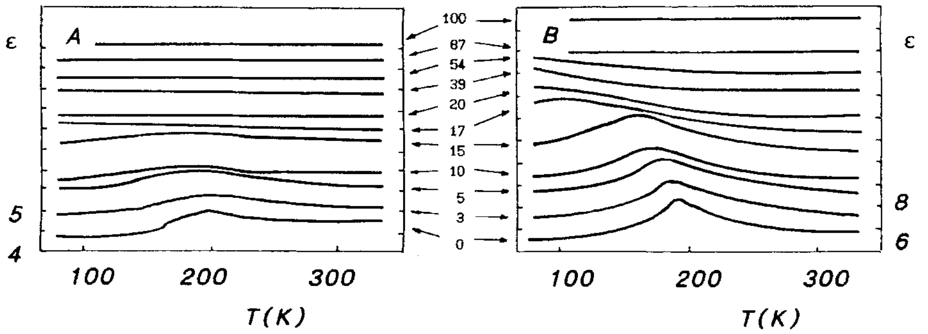


FIGURE 5 ε(T) dependences in monomer (A) and fully polymerized (B) pTS-pFBS mixed crystals. The numbers refer to the sample compositions expressed in mole % of pFBS. Note different ε scales in Figs. A and B. For the sake of clarity, the curves are vertically shifted by half of ε unit in A, and by one unit in B.

CONCLUSIONS

We studied the evolution of the photoelectric and dielectric properties of mixed pTS-pFBS single crystals. The main results are as follows:

- The kinetics of the polymerization is a function of the composition of the crystals, the rate constants in the induction and autocatalytic periods exhibiting different composition dependences.
- Changes in the kinetics of the photocurrent build-up essentially follow the changes in the polymerization kinetics, the model developed for pure pTS holding also for the mixed crystals.
- The phase transitions in the mixed crystals shift towards lower temperatures, probably due to weaker dipole-dipole interactions between side groups in pFBS.

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