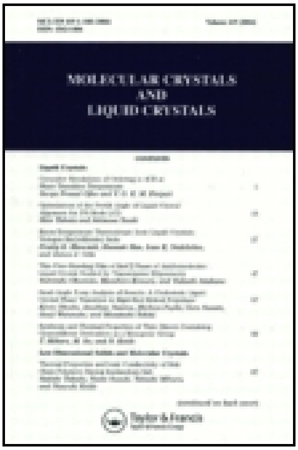


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Solid-State Polymerization of Disubstituted Diacetylenes

David Bloor [a]

[a] Department of physics, Queen Mary College, Mile End Road, London, E1 4NS, U.K.

To cite this article: David Bloor (1983): The Solid-State Polymerization of Disubstituted Diacetylenes, Molecular Crystals and Liquid Crystals, 93:1, 183-199

To link to this article: http://dx.doi.org/10.1080/00268948308073527

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 183–199
0026-8941/83/9304–0183/$18.50/0

Printed in the United States of America

THE SOLID-STATE POLYMERIZATION OF DISUBSTITUTED DIACETYLENES

DAVID BLOOR
Department of Physics, Queen Mary College,
Mile End Road, London E1 4NS, U.K.

Abstract The solid-state chemistry of disubstituted diacetylenes has attracted considerable attention because the product is, in certain cases, a macroscopic polymer crystal. In this review the topics discussed are (a) the criteria for solid-state reactivity and (b) studies of the reaction kinetics. Current models of reactivity and kinetics are presented in the light of the available experimental data.

INTRODUCTION

The solid-state reaction of disubstituted diacetylenes has been the subject of intensive research since the discovery by Wegner in 1969[1] that the reaction product can be a macroscopic polymer crystal. It is, therefore, probably the best documented solid-state reaction with detailed information available concerning the criteria for solid-state reactivity, the reaction kinetics and the reaction mechanism. In this review the last of these topics will not be discussed since it is the subject of a number of other contributions to this volume.

An extensive review of all three topics has appeared recently[2]. This contains references to earlier reviews most of which have been concerned with the physical properties of the product polymers. A brief history of studies of diacetylenes prior to 1969 was also presented and will not be repeated here. The emphasis here will be on more recent developments.

The basic reaction of disubstituted diacetylenes is as originally proposed by Hirschfeld and Schmidt[3] and leads to a conjugated polymer chain with a structure close to the idealised structure shown in Figure 1. The product polymer crystals have and will continue to attract interest as model materials since their relatively perfect crystal structure contrasts sharply with the complex amorphous and microcrystalline morphologies of other conjugated polymers currently attracting attention because of their high electrical conductivity[4]. This perfection is illustrated in Figure 2 and has been emphasized by the recent observation of TEM images resolving the polymer lattice structure[5]. The low density of lattice defects, observed in these studies of thin crystals, has also been shown to be a property of macroscopic crystals by the topographic studies described elsewhere in this volume.

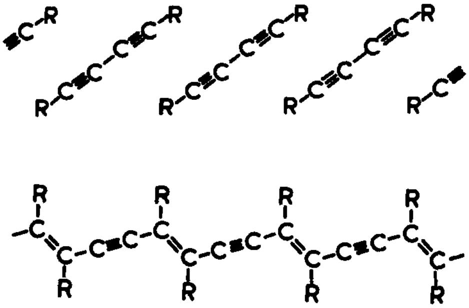


FIGURE 1. Schematic diagrams of a stack of reactive diacetylenes (above) and the product polymer chain (below).

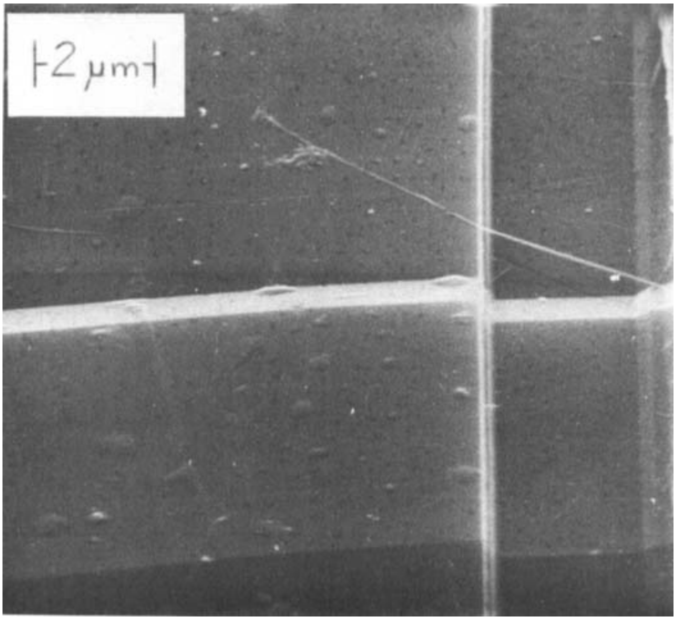


FIGURE 2. Scanning electron micrograph of TS crystal; the vertical feature is a channel left by a cleaved fibre, the horizontal feature is a stress twin.

The topographic studies are also significant from a chemical viewpoint. The observations that defect free regions of the crystal are uniformly polymerized and that there is no change in defect density during polymerization show that dislocations are not the only, or indeed the dominant, reaction site in diacetylene crystals. Thus, the solid-state reaction in diacetylenes must be a true topochemical reaction which can occur in the undeformed crystal lattice. This distinguishes it from many other solid-state topochemical reactions which can occur only in the vicinity of lattice defects. The reaction criteria and kinetics for diacetylenes are considered in more detail below.

CRITERIA FOR SOLID-STATE REACTION

Two models of the solid-state polymerization of diacetylenes have been discussed in the literature. The simpler model is that of Hirschfeld and Schmidt who considered a reaction, as shown in Figure 1, in which the diacetylene units were able to undergo a 1,4-polymerization simply by rotation with their centres of gravity on fixed lattice sites[3]. Under such conditions the empirical criterion due to Schmidt[6], that the reacting carbons must have a separation of less than 0.4 nm in the monomer lattice, should apply. As will be seen below the restriction of zero lateral displacement during reaction is rarely satisfied. Despite this Schmidt's simple criterion may still apply since the internal strain developed in materials with large monomer-polymer mismatch are likely to affect kinetics and product perfection but not prevent the polymerization reaction from occuring.

The second model, due to Baughman[7], allows for both rotation and translation of the diacetylene units which are assumed to behave as rigid rods. In this model the root-mean-square displacements of the diacetylene units were calculated assuming (a) a simultaneous translation and rotation and (b) a pure translation i.e. a shearing motion of the reacting units. In both cases the motion was constrained to the plane containing the diacetylene units. The shearing motion was found to give larger r.m.s. displacements. Experimentally the polymer chains are observed to coincide with the axis of the monomer stack in accord with this result.

These models can be compared by drawing the contours for 1,4-carbon separation of 0.4 nm (D) and an arbitrary chosen r.m.s. displacement of 0.1 nm (R) in a space with co-ordinates equal to the separation of the centres of gravity of the diacetylenes along the stack axis (d) and the angle between the axes of the diacetylene units and the stack axis (γ). Such a plot is shown in Figure 3. The dash and chain lines show the limiting values of D and R respectively. For reaction the d and γ values must lie to the left of these curves. Not all values of d and γ are allowed since the diacetylene units cannot

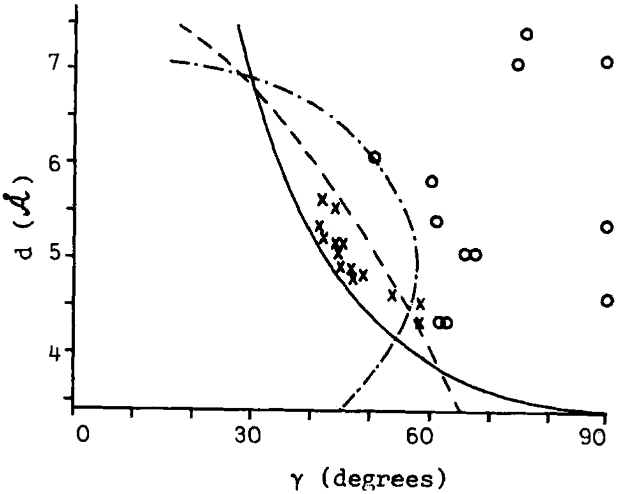


FIGURE 3. Diacetylene monomer packing and reactivity. See text for definition of variables and symbols.

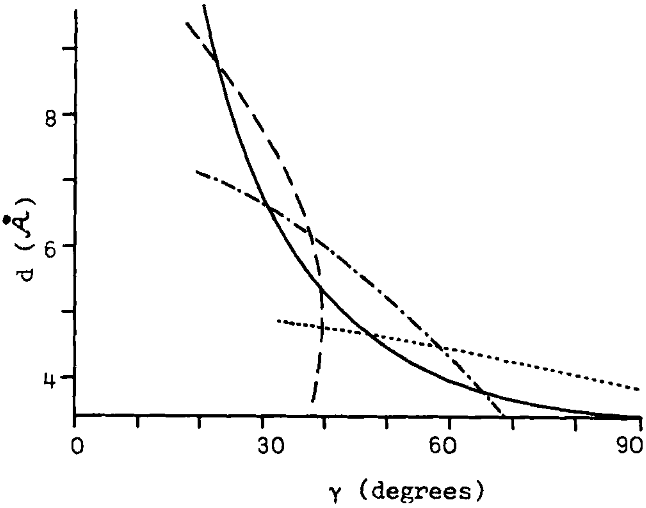


FIGURE 4. Bounds for reactions of mono- (dotted curve), di- (chain curve) and tri-acetylenes (dash curve). The solid curve is limit set by closest packing of monomers.

approach closer than twice the van der Waals radii of the acetylenic carbons. This limit is shown by the full curve in Figure 3, with possible d and γ values being to the right of this curve.

Values of d and γ obtained from X-ray structural analyses of diacetylenes[2,8], are plotted in Figure 3. Crosses represent reactive monomers and circles unreactive monomers. Though the data is not absolutely conclusive the only X significantly outside the D 0.4 nm bound is a monomer which polymerizes under shear so that the use of undistorted lattice values is probably in error. Thus, Schmidt's criterion can be used as a reasonable guide to the solid-state reactivity of diacetylenes. It should be noted that the assumptions of the least-motion model are too severe. A reaction path involving-out-of-plane motion is suggested by calculations of least-energy paths for methylene radicals[9]. Recently a low-lying phonon mode has been shown to be important in the polymerization of one diacetylene though its exact nature has not been identified[10]. Both these facts indicate that molecular deformation occurs during reaction so that a model involving planar motion of rigid rods is not realistic.

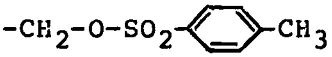
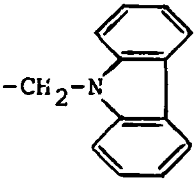
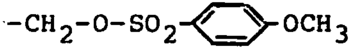
Schmidt's criterion can be used to obtain estimates of the d and γ values required for 1,2-reaction of monoacetylenes and 1,6 reaction of triacetylenes, as shown in Figure 4. Little data is available for comparison with these predictions. It is likely, however, that tri- and diacetylenes with similar sidegroups will have similar lattice packing and similar d and γ values. Thus, a 1,4-reaction will be favoured for tri-acetylenes as observed experimentally[11]. Solid-state reactions of mono-acetylenes reported in the literature do not appear to be topochemical in nature[12].

The use of Schmidt's criterion to predict the reactivity of disubstituted diacetylenes has been limited by the large size of the molecules and their flexibility. This means that in principle lattice structures would have to be calculated for several different conformations. The large number of atoms involved together with the limited information on internal energy and the inaccuracy of available potential functions means that accurate crystal free energies cannot be calculated even for known structures[2,8]. Thus, it appears that it will be some time before reactive diacetylenes can be 'designed' on anything other than an empirical basis. It should be noted, however, that the inverse is possible, i.e. the reaction criterion can be used to obtain reasonable models of the crystal structures of diacetylenes not amenable to X-ray diffraction techniques[13].

REACTION KINETICS

In general it is observed that the reactive diacetylenes which produce good polymer crystals have large substituent groups[14]. This follows since in addition to being the principal agent in determining the monomer lattice packing, and hence the reactivity, they must ensure a unique reaction direction and mediate the strain between the initially formed polymer and the monomer matrix. This internal strain can be quite large as seen by comparing the d values of Figure 3 with the size of the repeat unit of the polymer of 0.491 nm. If the internal strain is too large subsequent polymerization occurs adjacent to the initial polymer and a heterogeneous polymerization with phase segregation occurs[15]. Conversely if the strain is small or distributed more uniformly through the lattice then the polymerization will proceed homogeneously[15]. In the former case the physical properties of the polymerizing monomer will change discontinuously and in the latter case the change will be continuous.

TABLE I Chemical compositions of the end groups of symmetrically substituted diacetylenes discussed in the text

Substituent Group	Abbreviation
	TS
	DCH
$-CH_2-O-CO-NH-C_2H_5$	ETU
	MBS

The best known example of homogeneous, or nearly homogeneous, polymerization is TS (see Table 1). The crystal dimensions[16,17], the elastic constants[16,18], the vibrational frequencies[19] and optical absorption[20] of the polymer have all been observed to change continuously during polymerization. Figure 5 shows recent measurements of the change in thermal expansion coefficient of TS crystals during polymerization[21]. All these measurements indicate that the polymer and monomer are under equal strain in the partially polymerized matrix, i.e. the Voight condition applies[22]. The solid curve in Figure 5 was calculated in this limit for a ratio of polymer to monomer elastic constants of five.

The polymerization curve for TS, Figure 6, shows, however, a sigmoid form characteristic of an autocatalytic process such as defect nucleation for a reaction at defect sites. Topographic studies show a constant defect density so that a defect mechanism is not operative in TS. A model which gives a good fit to the polymerization data has been proposed by Baughman[23]. This supposes that the energy barriers for initiation and chain propagation are determined by the elastic strain required to deform the lattice adjacent to the reacting monomer, the overall lattice strain being determined by the Voight condition. A number of approximations are necessary to render the problem tractable; these have been discussed elsewhere[2]. From the variation in crystal dimensions the ratio of polymer and monomer elastic constants was

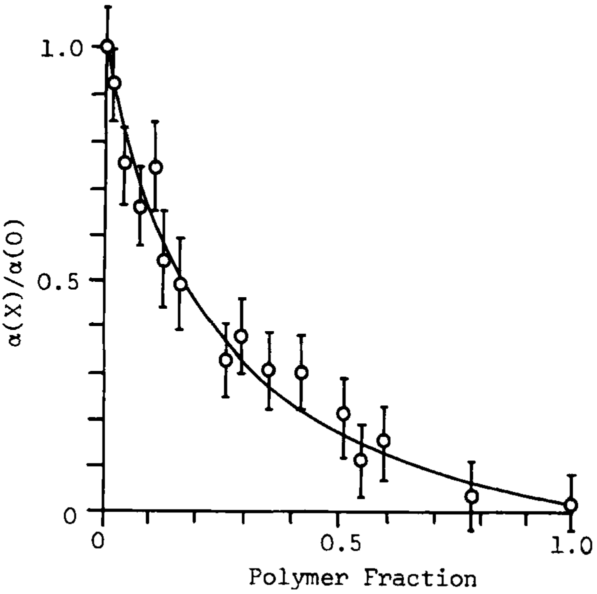


FIGURE 5. Variation in thermal expansion coefficient of TS crystals during polymerization.

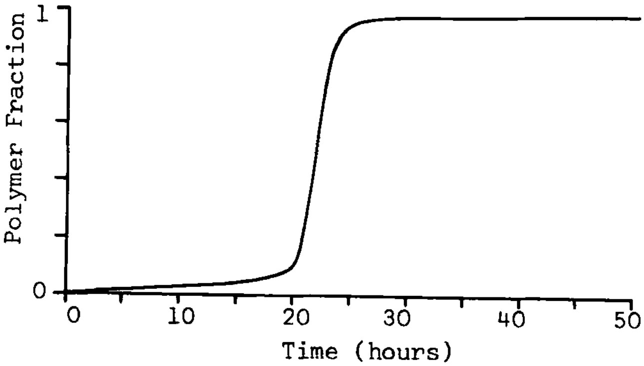


FIGURE 6. Conversion versus time for the thermal polymerization of TS at 273 K.

deduced to be 4.66 close to the experimental value determined by Brillouin scattering[16]. Calculation using this ratio gave an excellent fit to the experimental data[23]. The prediction of this model of an increase in kinetic polymer chain length has been confirmed by diffuse X-ray scattering[24].

Despite this success the model has been questioned in the light of polymerization studies of TS under high pressure[25], with isotopic substitution[26] and the related monomer MBS[27]. Different reasons have been adduced for the apparent discrepancies between this data and the lattice-strain model[28]. The changes in shape of the polymerization curve under pressure and with isotopic substitution were attributed to defects acting as chain termination sites. It seems unlikely, however, that the necessary differences in defect densities required[28] would occur reproducibly from sample to sample. Furthermore this explanation would require the form of the polymerization curve to be dependent on composition for co-crystallized momoners where one component is unreactive; experimental observations show a universal form to occur[29]. In the case of MBS a much larger effective elastic constant ratio was invoked to explain the absence of an induction period[28]. This appears improbable in view of the similar changes in lattice dimensions observed for TS and MBS[8]. The recent observation of an elastic constant ratio for TS of 6.5[18] raises further doubts concerning the validity of the simple lattice-strain model.

Further progress in the understanding of the kinetics of homogeneously-polymerizing diacetylenes required a more detailed consideration of the initiation process. Little is currently known about the way energy is transferred to or may be trapped at the site of initiation. In addition though the averaged lattice strain is homogeneous local variations in strain occur[19,30], the effects of these on the polymerization kinetics have not been considered.

Very similar polymerization kinetics can occur for less ideal polymerization; two examples are DCH and ETU. In the case of DCH an autocatalytic kinetic has been shown to occur as the result of a phase transition induced by the lattice strain[31,32]. This is a coherent transition since the final polymer has a single structure[32]. The polymerization of ETU, Figure 7, is well described by the lattice-strain model but is in fact a two phase polymerization in which lattice strain causes inhomogeneous nucleation of a second phase[13]. In such cases the kinetics can be described by a simple model in which polymerization proceeds by first-order kinetics in both phases but with different rate constants. Then for a material in which the two phases co-exist between polymer fractions X(1) and X(2) the polymerization rates will be given by:

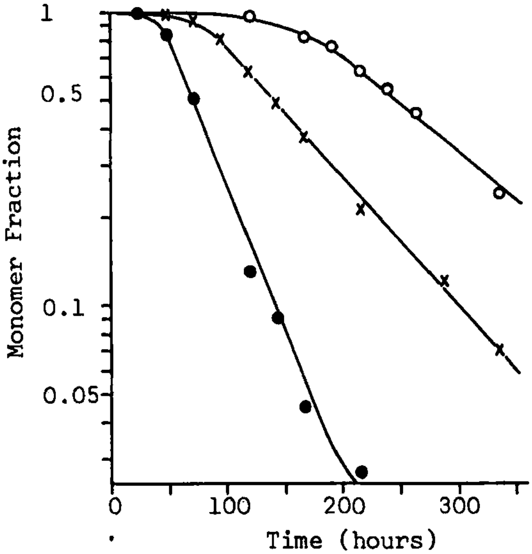


FIGURE 7. Semilog plot of momoner fraction versus time for ETU thermal polymerization at 343 K (O), 353 K (X) and 358 K (●).

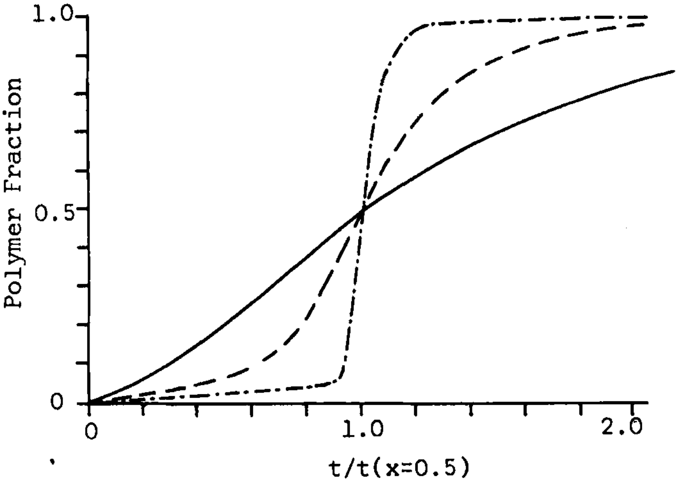


FIGURE 8. Calculated polymerization curves for a 2 phase system with k_2/k_1 3 (solid curve), 30 (dash curve) & 250 (chain curve).

$$R = (1-X).k_1 \qquad X < X(1)$$

$$R = (1-X)\left[\frac{X-X(1)}{X(2)-X(1)}.(k_2-k_1)-k_1\right] \qquad X(1) < X < X(2)$$

$$R = (1-X).k_2 \qquad X(2) < X$$

Results for different ratios of the rate constants, when $X(1) = 0.05$ and $X(2) = 0.4$, are plotted in Figure 8. These expressions give good fits to the experimental data for DCH and ETU with reasonable values of the parameters $X(1)$, $X(2)$, k_1 and k_2.

CONCLUSIONS

Diacetylene solid-state polymerization is a well established area of solid-state chemistry. Challenges remain, however, in determining more precisely the relationship of monomer structure and reactivity, so that new materials can be produced in a systematic and controlled manner, and in refining the models of polymerization kinetics. The striking physical properties of the resultant diacetylene polymers are currently being investigated for device applications. This, and the use of polydiacetylene polymer crystals as model systems for fundamental investigation, will ensure continued activity in this branch of solid-state chemistry.

ACKNOWLEDGEMENTS

This research was supported by grants from the Science and Engineering Research Council. Members of the Polymer Research Group at Queen Mary College are thanked for useful discussions.

REFERENCES

1. G. Wegner, Z. Naturforsch, 24b, 824 (1969).
2. D. Bloor, in Developments in Crystalline Polymers-1, edited by D.C. Bassett (Applied Science Publishers, London, 1982) p.151.
3. F.L. Hirschfeld and G.M.J. Schmidt, J.Polymer Sci. A, 2, 2181 (1964).
4. G. Wegner, Angew. Chem. Int. Ed. Engl., 20, 361 (1981).
5. R.T. Read and R.J. Young, J. Mater. Sci., 16, 2922 (1981).
6. G.M.J. Schmidt, in Reactivity of the Photo-excited Organic Molecule (J. Wiley, New York, 1967) p.227.
7. R.H. Baughman, J. Polym. Sci. Polymer Phys. Ed., 12, 1511 (1974).
8. R.L. Williams, Thesis, Univ. of London (1982).
9. R. Hoffmann, R. Gleiter and F.B. Mallory, J. Amer. Chem. Soc., 92, 1460 (1970).
10. H. Niederwald, Thesis, Univ. of Bayreuth (1982).
11. J. Kiji, J. Kaiser, G. Wegner and R.C. Shultz, Polymer, 14, 433 (1973).
12. O. Rohde and G. Wegner, Makromol. Chem., 179, 2013 (1978).
13. C. Galiotis, R.J. Young, D.J. Ando and D. Bloor, Makromol. Chem., in press.
14. D. Bloor, Springer Lect. Notes in Phys., 113, 14 (1980)
15. J. Kaiser, G. Wegner and E.W. Fischer, Israel J. Chem., 10, 157 (1972).
16. V. Enkelmann, R.J. Leyrer and G. Wegner, Makromol. Chem., 180, 1787 (1980).

17. K. Lochner and H. Bassler, Ber. Bunsenges. Phys. Chem., 84, 880 (1980)
18. W. Rehwald, A. Volanthen and W. Meyer, to be published.
19. D. Bloor, R.J. Kennedy and D.N. Batchelder, J. Polymer Sci. Polymer Phys. Ed., 17, 1355 (1979)
20. D. Bloor, R.L. Williams and D.J. Ando, Chem. Phys. Lett., 78, 67 (1981).
21. D. Bloor, R.J. Day and M. Motevalli, to be published.
22. W. Voight, Lehrbuch der Kristallphysik, (Tuebner, Berlin, 1910).
23. R.H. Baughman, J. Chem. Phys., 68, 3110 (1978).
24. P.A. Albouy, P. Keller and J.P. Pouget, to be published.
25. K. Lochner, H. Bassler and T. Hinrichsen, Ber. Bunsenges. Phys. Chem., 83, 899 (1979).
26. C. Kronke, V. Enkelmann and G. Wegner, Chem. Phys. Lett., 71, 38 (1980).
27. D. Bloor, D.J. Ando, C.L. Hubble and R.L. Williams, J. Polymer Sci. Polymer Phys. Ed., 18, 779 (1980).
28. R.H. Baughman and R.R. Chance, J. Chem. Phys., 73, 4113 (1980).
29. V. Enkelmann, J. Mater. Sci., 15, 951 (1980).
30. W. Hoptner, J.U. von Schutz and H.C. Wolf, J. Polymer Sci. Polymer Phys. Ed., 18, 469 (1980).
31. K.C. Yee and R.R. Chance, J. Polymer Sci. Polymer Phys. Ed., 16, 431 (1978).
32. V. Enkelmann, R.J. Leyrer, G. Schleier and G. Wegner, J. Mater. Sci., 15, 168 (1980).