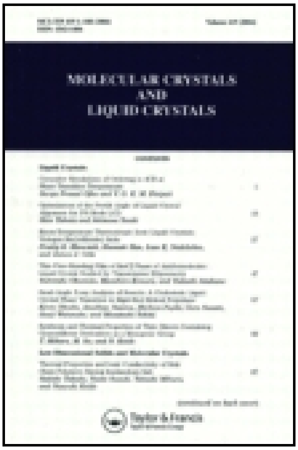

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Secondary Chain Initiation During Thermal and Photopolymerization of PTS

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SECONDARY CHAIN INITIATION DURING THERMAL AND PHOTO-POLYMERIZATION OF PTS

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Abstract From an analysis of the reaction kinetics of PTS it is concluded that secondary chain initiation, previously postulated on the basis of photopolymerization studies under spatially inhomogeneous irradiation, is also important in course of thermally induced polymerization.

Recent experimental work on photopolymerization of diacetylene-bis(toluenesulfonate) (TS) under hydrostatic pressure provided evidence for secondary chain initiation[1]. A virgin TS crystal, mounted in a high pressure cell, had been irradiated by UV light through a mica mask containing about 7000 rhombic holes per cm^2 with an edge length of 10 μm. After chemical etching the profile of the polymerization zone was analyzed microscopically. The essential observations were:

(i) With increasing pressure polymerization extends into unirradiated crystal areas.

(ii) Growth of the polymerization zone is almost isotropic within the (100) plane.

(iii) At 4 kbar the crystal surface becomes fully polymerized. This implies polymer growth across distances of the order 30 μm into unirradiated sample areas.

Since a single polymer chain can only propagate along |010| and, further, since some 10 µm is an unrealistically large value for the length of an individual chain, we had to postulate that a running chain initiates secondary chains in its neighborhood. As an explanation we proposed that motion of the CH_2-group between diacetylene moiety and substituent, which is excited in course of the 1,4 addition reaction, induces a librational motion of a TS monomer in an adjacent molecular stack. Thereby the reaction distance is temporarily shortened and a new polymer chain can be initiated without requiring the full amount of the thermal activation energy necessary to initiate a primary chain. Since secondary chains are generated along [001] and propagate along |010|, the secondary polymerization effect is expected to display little if any anisotropy within the (100) plane.

Creation of a secondary chain must be independent of whether the primary chain has been initiated thermally or optically. A crucial test for the validity of the above concept is therefore its applicability to thermal polymerization of TS which can formally be described by a first order rate equation, $d|M|/dt = -K|M|$. $|M|$ is the monomer concentration and K is proportional to the number of monomers converted to polymer per primary initiation event. In the autocatalytic reaction regime K increases with conversion. In figure 1 K-data taken from the literature[2] are plotted as a function of the lattice mismatch $\Delta b = b(c_p)-b(c_p=0)$, where $b(c_p)$ is the lattice parameter along |010| at a fractional polymer conversion c_p[3] and $b(c_p=0)$ is the corresponding parameter of the monomer lattice. Δb is proportional to the change of the C1-C4 distance as the reaction proceeds. Near $\Delta b = -0.1$ Å, $K(\Delta b)$ displays a sharp increase by more than one order of magnitude and approaches an exponential law at

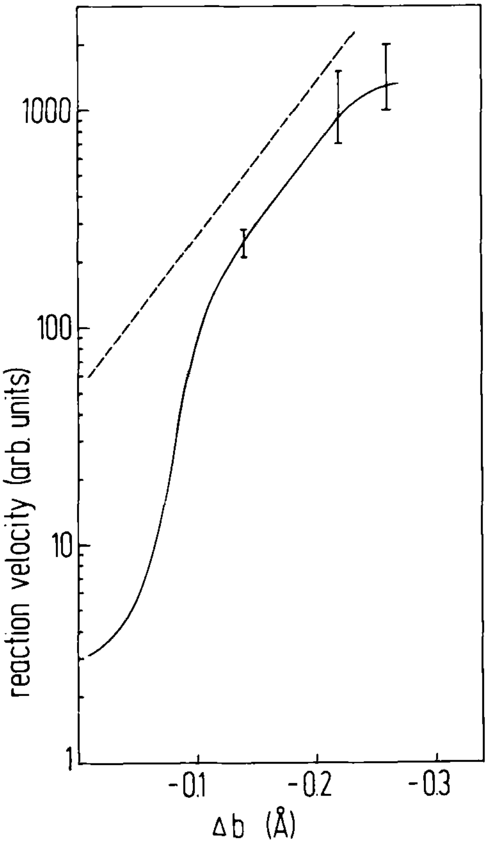

FIGURE 1. Reaction velocity, normalized to the concentration of reactive monomer (in the text denoted by K) as a function of the lattice mismatch Δb (for definition see text). The dashed curve is the correlation between K and Δb derived from thermal polymerization under hydrostatic pressure[4].

larger -Δb values.

Previous pressure work[4] indicated that K increases under hydrostatic pressure according to $K(p) = K(p=0)\exp(p/p_o)$ with $p_o = 1.68$ kbar. Converting pressure to lattice contraction along [010] [4] allows expressing K(p) in terms of pressure-induced lattice contraction. Figure 1 shows that at large $-\Delta b$-values the slopes of lnK vs. Δb graphs obtained from either thermal conversion studies at 1 bar or high pressure work are virtually identical. This demonstrates the crucial role of the reaction distance for polymerization of TS, at least in the high conversion limit.

If the total enhancement of K were due to an increase in chain length, $n_{max}/n_{oo} \simeq 300$ would follow, where n_{max} and n_{oo} denote the degree of polymerization at maximum reaction rate and in the $c_p \to 0$ limit, respectively. Inserting $n_{oo} \simeq 20$[5,6] would yield $n_{max} \simeq 6000$, for the reaction at 1 bar, equivalent to a chain length of 3 µm. At p = 6 kbar $n_{max} \simeq 2 \cdot 10^5$ would come out. Both values are incompatible with the single chain concept. Wenz and Wegner[7] reported $\langle n_{max} \rangle \simeq 1000$ for polymerization of TS12 at 1 bar with the indication of an increase by only a factor of 2 at 4 kbar. We therefore conclude that more than one chain must be formed per thermally induced primary chain initiation center. In the following a simple model is outlined that is able to explain the reaction induced increase of the reaction rate constant K on the basis of both an increase of the average length of an individual chain, as has been proposed by Baughman[2], and a reaction dependent secondary chain formation.

Let q be the probability that the energy released per addition of a TS monomer to a running polymer chain is used to initiate a secondary chain. Then the total number of secondary chains is $N = (1-qn)^{-1}$ and the total number of monomers consumed per primary initiation event is $n_c = Nn$. Here n is the number of monomers contained in an individual polymer chain at a given conversion c_p. Since $K \sim Nn$, $q(\Delta b)$ can be inferred from existing $K(\Delta b)$-data provided the chain length is known as a function of conversion. The curves presented in figure 2 are calculated on the assumption that (i) the

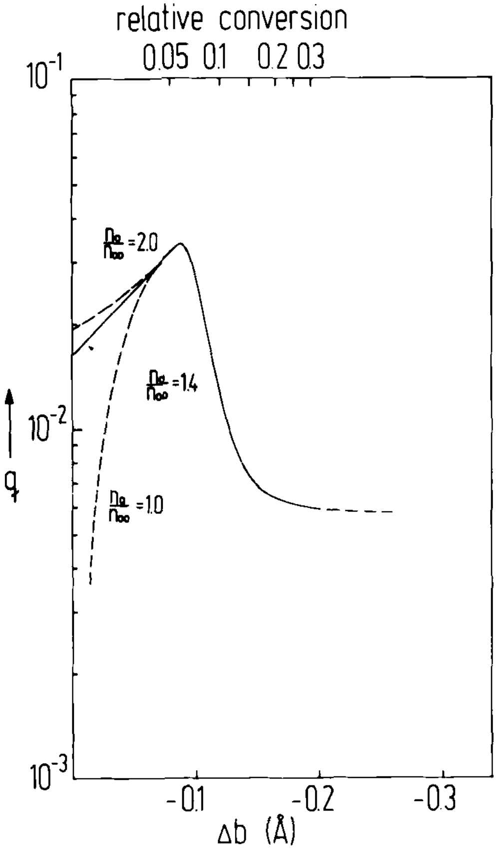

FIGURE 2. Probability that a running chain initiates a secondary chain as a function of Δb. Parameter is the ratio of the number of reacted monomer molecules per primary chain initiation event to the number of monomers contained within a single chain in the zero conversion limit.

increase in the length of an individual chain follows the predictions of Baughman's elastic strain theory[2] and (ii) that $n_{oo}=20$ [5,6]. Parameter is $N(c_p \to 0) = (n_o/n_{oo})_{c_p \to 0}$, where $n_o = n_c(c_p \to 0)$. q turns out to be of the order 10^{-2}. It increases at low conversion and decreases above $c_p \simeq 0.1$. The drop at higher c_p is expected to occur since with increasing conversion the probability for secondary chain initiation must decrease as a consequence of the blocking effect exerted by chains already existing in the vicinity of a running chain.

The probability for formation of a covalent bond between the C1 and C4 atoms of adjacent monomers should be proportional to the overlap of the π-electron wave functions of the reactive centers which is determined by $\exp(-2\alpha s)$, α being the wavefunction decay parameter and s the reaction distance. For $N(c_p \to 0) = 1.4$, the calculated $q(\Delta b)$ curve is in fact an exponential function of Δb yielding $\alpha \simeq 5$ Å^{-1}. This is of the correct order of magnitude (the decay constant of the Slater functions for a ground state carbon atom is about 2.5 Å^{-1} [8]).

In principle the concept of secondary chain initiation is at variance with the generally adopted view of purely statistical polymer growth within the monomer matrix[9]. However, at low conversion the number of secondary chains created per primary chain is only of the order of one, too low to give rise to any measurable chain correlation effect in a diffraction experiment[10,11]. In the high conversion limit, where the number of secondary chains is of the order 10, the question of chain correlation becomes irrelevant, since a new chain will in practice always be initiated in the vicinity of an already existing chain, irrespective of the initiation mechanism.

In conclusion, the concept of secondary chain initiation, originally invoked to explain photopolymerization data, removes the discrepancy between the degree of polymerization determined chromatographically and the value required to fit thermal conversion data. Since it is based on coupling between adjacent stacks of diacetylene monomers via side group motion the normal isotope effect reported by Kröhnke et al.[12] may find a plausible explanation.

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